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INORGANIC HALOGEN OXIDIZER RESEARCH  
(1 January 1976 through 31 December 1976)

4 February 1977

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| 20. ABSTRACT (Continue on reverse side if necessary and identify by block number)<br>The novel $NF_4^+$ salts $(NF_4)_2NiF_6$ , $(NF_4)_2TiF_6$ , $NF_4Ti_2F_9$ , $NF_4Ti_3F_{13}$ , $NF_4Ti_6F_{25}$ , and $NF_4SnF_5$ were synthesized and characterized. The $(NF_4)_2NiF_6$ and $(NF_4)_2TiF_6$ salts are of significant interest as ingredients in solid propellant $NF_3-F_2$ gas generators for chemical HF-DF lasers. The nickel salt represents the first successful combination of both an energetic perfluoro cation and anion in the form of a stable salt. The theoretical usable fluorine content of this salt is 68 percent higher than that obtainable with KF clinkered $NF_4BF_4$ , the best previously known |                       |  |

## 20. ABSTRACT (continued)

system. On thermal decomposition, one cm<sup>3</sup> of solid (NF<sub>4</sub>)<sub>2</sub>NiF<sub>6</sub> is capable of producing 1.5 times as much useful fluorine, i.e. in the form of NF<sub>3</sub> and F<sub>2</sub>, as liquid F<sub>2</sub> at -187 C. The metathetical NF<sub>4</sub>BF<sub>4</sub> process was refined and high purity (> 99%) metathetical NF<sub>4</sub>BF<sub>4</sub> was obtained for the first time, thus eliminating the major drawback of the metathetical route. The process for the synthesis of the NF<sub>4</sub>SbF<sub>6</sub> starting material was also improved by elimination of the cumbersome vacuum pyrolysis step. The usefulness of solid propellant NF<sub>3</sub>-F<sub>2</sub> gas generators for the rapid destruction of magnetic tape was demonstrated. Information was obtained on the intermediates formed in the uv photolytic synthesis of NF<sub>4</sub>BF<sub>4</sub>. It was shown by esr spectroscopy that the BF<sub>4</sub> radical is formed as the key intermediate during the low-temperature, uv-photolysis of the NF<sub>3</sub>-F<sub>2</sub>-BF<sub>3</sub> system. The ESCA spectrum of NF<sub>4</sub>BF<sub>4</sub> has been measured.

In the field of halogen fluorides the reactions of KClO<sub>3</sub> with ClF<sub>5</sub> and of MBrO<sub>4</sub> with BrF<sub>5</sub> were studied. No novel compounds were obtained. Unsuccessful attempts were made to prepare the novel ClF<sub>4</sub>O radical by γ-irradiation of ClF<sub>3</sub>O in SF<sub>6</sub> matrix at -196 C.

Normal coordinate analyses of SF<sub>5</sub>Br and SF<sub>4</sub>O were carried out. Attempts to prepare O<sub>2</sub><sup>+</sup>ClO<sub>4</sub><sup>-</sup> by metathesis were unsuccessful. Evidence for the formation of the novel perchlorate W(ClO<sub>4</sub>)<sub>6</sub> was obtained, however this compound appears to be unstable. Attempts to synthesize the novel WF<sub>6</sub><sup>+</sup> and MoF<sub>6</sub><sup>+</sup> cations were unsuccessful. The usefulness of the recently discovered stable oxonium salts as polymerization catalysts was demonstrated.

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## FOREWORD

The research reported herein was supported by the Office of Naval Research, Power Branch, Code 473, with Dr. R. S. Miller as Scientific Officer. This report covers the period 1 January 1976 through 31 December 1976. The program has been directed by Dr. K. O. Christe. The scientific effort was carried out by Drs. K. O. Christe, C. J. Schack, and Mr. R. D. Wilson. The program was administered by Dr. L. Grant, Manager, Exploratory and Analytical Chemistry, and Dr. K. O. Christe, Program Engineer.

## INTRODUCTION

This report covers a 12-month period and describes Rocketdyne's research efforts in the area of halogen chemistry. As in the past years, our research was kept diverse and covered areas ranging from the exploration of new synthetic methods and the syntheses of novel compounds to structural studies. However because of the importance of  $\text{NF}_4^+$  salts as ingredients for solid propellant  $\text{NF}_3\text{-F}_2$  gas generators for chemical HF-DF lasers, our main efforts were concentrated in this area. The existence of stable  $\text{NF}_4^+$  salts was originally discovered by one of us in 1965 (Ref. 1) under ONR sponsorship, and much of the development in this field has since been achieved at Rocketdyne under this ONR program.

Particular progress in the field of solid propellant  $\text{NF}_3\text{-F}_2$  gas generators was made by us during the current program year. Thus, the novel  $\text{NF}_4^+$  salts  $(\text{NF}_4)_2\text{SnF}_6$ ,  $(\text{NF}_4)_2\text{TiF}_6$ , and  $(\text{NF}_4)_2\text{NiF}_6$  were discovered, and the concept of self-clinkering formulations was developed. The nickel salt is of particular importance since it constitutes the first known combination of an energetic perfluoro cation with an energetic perfluoro anion in the form of a stable salt. In this manner, we have succeeded to boost within one year the theoretically achievable fluorine yield from 38.5 weight % (for clinkered  $\text{NF}_4\text{BF}_4$ ) to 64.6% for  $(\text{NF}_4)_2\text{NiF}_6$ .

The results obtained under this program have been successfully applied to a number of past and ongoing Navy, Army, and Air Force programs, thus demonstrating the usefulness of goal-oriented basic research.

As in the past (Ref. 2), we have summarized completed pieces of work in manuscript form suitable for publication. Thus, time spent for report and manuscript writing is minimized, and widespread dissemination of our data is achieved.

During the past 12 months, the following papers were published, submitted for publication, or presented at meetings. In addition, several patents were either issued or filed. All of these arose from work sponsored under this program.

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## PUBLICATIONS AND PATENTS DURING PAST CONTRACT YEAR

### Papers Published

1. "On the  $\text{PtF}_6\text{-XeOF}_4$  Reaction System," K. O. Christe and R. D. Wilson, J. Fluor. Chem., 7, 356 (1976).
2. "Chlorine Oxyfluorides," by K. O. Christe and C. J. Schack, Advanc. Inorg. Chem. Radiochem., 18, 319 (1976).
3. "Some Observations on the Reaction Chemistry of Dioxygenyl Salts and on the Blue and Purple Compounds Believed to be  $\text{ClF}_3\text{O}_2$ ," K. O. Christe, R. D. Wilson and I. B. Goldberg, J. Fluor. Chem., 7, 543 (1976).
4. "Titanium Tetraperchlorate and Chromyl Perchlorate," C. J. Schack, D. Pilipovich and K. O. Christe, J. Inorg. Nucl. Chem., Supplem., 207 (1976).
5. "Low-Temperature Ultraviolet Photolysis and its Application to the Synthesis of Novel and Known  $\text{NF}_4^+$  Salts," K. O. Christe, C. J. Schack and R. D. Wilson, Inorg. Chem., 15, 1275 (1976).
6. "Vibrational Spectra of the Trigonal Bipyramidal Tetrafluorides  $\text{SF}_4$  and  $\text{ClF}_4^+$ ," K. O. Christe, E. C. Curtis and C. J. Schack, Spectrochim. Acta, 32A, 1141 (1976).
7. "Dioxygenyl Pentafluorogermanate (IV),  $\text{O}_2^+\text{GeF}_5^-$ ," K. O. Christe, R. D. Wilson and I. B. Goldberg, Inorg. Chem., 15, 1271 (1976).
8. "Vibrational Spectrum and Force Constants of the  $\text{XeF}_5^+$  Cation," K. O. Christe, E. C. Curtis and R. D. Wilson, J. Inorg. Nucl. Chem., Supplem., 159 (1976).
9. "Fluoride Crystal Structures. Part XXVI. Bis[di-fluorobromonium (II)] Hexafluorogermanate (IV)," A. J. Edwards and K. O. Christe, J. Chem. Soc. Dalton, 175 (1976).
10. "trans-Dihydridotetrafluorophosphate (V) Anion,  $\text{trans-H}_2\text{PF}_4^-$ ," K. O. Christe, C. J. Schack and E. C. Curtis, Inorg. Chem., 15, 843 (1976).
11. "Improved Syntheses of  $\text{NF}_4\text{BF}_4$  and  $\text{NF}_4\text{SbF}_6$ ," K. O. Christe, C. J. Schack and R. D. Wilson, J. Fluor. Chem., 8, 541 (1976).



#### Papers in Press

12. "On the Synthesis and Characterization of  $\text{NF}_4\text{BiF}_6$  and Some Properties of  $\text{NF}_4\text{SbF}_6$ ," K. O. Christe, R. D. Wilson and C. J. Schack, Inorg. Chem.
13. "Synthesis and Characterization of  $(\text{NF}_4)_2\text{SnF}_6$  and  $\text{NF}_4\text{SnF}_5$ ," K. O. Christe, C. J. Schack and R. D. Wilson, Inorg. Chem.
14. "Synthesis and Characterization of  $(\text{NF}_4)_2\text{TiF}_6$  and of Higher  $\text{NF}_4^+$  and  $\text{Cs}^+$  Polyperfluorotitanate (IV) Salts," K. O. Christe and C. J. Schack, Inorg. Chem.
15. "Synthesis and Characterization of  $(\text{NF}_4)_2\text{NiF}_6$ ," K. O. Christe, Inorg. Chem.
16. "Vibrational Spectrum and Normal Coordinate Analysis of  $\text{SF}_5\text{Br}$ ," K. O. Christe, E. C. Curtis, C. J. Schack and A. Roland, Spectrochim. Acta.
17. "Vibrational Spectra of Thionyl Tetrafluoride,  $\text{SF}_4\text{O}$ ," K. O. Christe, C. J. Schack and E. C. Curtis, Spectrochim. Acta.

#### Papers Presented at Meetings

18. " $\text{NF}_4^+$  Chemistry," K. O. Christe, C. J. Schack and R. D. Wilson, 8th International Symposium on Fluorine Chemistry, Kyoto, Japan (August 1976).
19. "Recent Progress in the Chemistry of  $\text{NF}_4^+$  Salts," C. J. Schack, K. O. Christe, R. D. Wilson and R. I. Wagner, 172nd ACS National Meeting, San Francisco (August 1976).
20. Invited seminars on "Energetic Halogen Chemistry" were given at Harvard-MIT, University of Arizona, Tucson, and the Science Center of Rockwell International.

#### Issued Patents

21. "Stable Unsubstituted Sulfonium Salts," K. O. Christe, U.S.P. 3,987,152 (October 19, 1976).

#### Filed Patents

22. "Germanium Containing  $\text{NF}_4^+$  Salts and Process for Preparing Same," K. O. Christe and C. J. Schack.

23. "Photolysis Method for Producing  $\text{NF}_4\text{PF}_6$ ," K. O. Christe and C. J. Schack.
24. "Displacement Reaction for Producing  $\text{NF}_4\text{PF}_6$ ," K. O. Christe and C. J. Schack.
25. "High Energy Solid Propellant Oxidizer and Method of Producing Same," K. O. Christe.
26. "Self-Clinkering  $\text{NF}_4^+$  Compositions for  $\text{NF}_3\text{-F}_2$  Gas Generators and Method of Producing Same," K. O. Christe, C. J. Schack and R. D. Wilson.

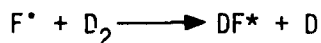
## DISCUSSION

### $\text{NF}_4^+$ CHEMISTRY

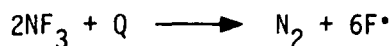
$\text{NF}_4^+$  salts, first discovered by one of us in 1965 under an ONR contract at Stauffer Chemical (Ref. 1), are the most promising oxidizers for solid propellant  $\text{NF}_3$ - $\text{F}_2$  gas generators. The concept of such a gas generator was conceived (Ref. 3) and to a large extent (Ref. 4 through 8) developed at Rocketdyne. It offers significant logistics and safety advantages over cryogenic or storable liquid oxidizers for use in chemical HF-DF lasers, for example. In a chemical HF-DF laser, F atoms are generated by burning  $\text{F}_2$  in a precombustor with a fuel, such as hydrogen:



The F atoms are subsequently reacted with a cavity fuel, such as  $\text{D}_2$ , to produce vibrationally excited DF as the active lasing species:

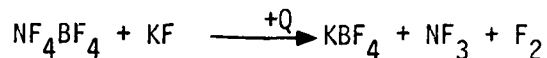


In the original solid F atom generator concept (Ref. 3), the F atoms were directly generated by burning the solid propellant grain, thus eliminating the need of a precombustor. This concept is demonstrated for  $\text{NF}_4\text{BF}_4$  with a small percentage of Teflon serving both as a fuel and a binder. The heat of reaction (Q) is sufficient to dissociate most of the  $\text{NF}_3$  and  $\text{F}_2$  to F atoms and  $\text{N}_2$ :



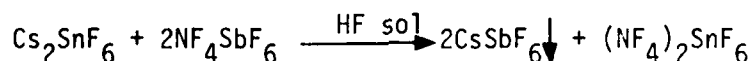
From a practical point of view, however, such a direct generation of F atoms is not desirable, since it does not allow the necessary flow controls and flexibility required for operation. Consequently, the concept was modified to that of an  $\text{NF}_3$ - $\text{F}_2$  molecule generator, using a gas catch tank. Further modification of this

concept became necessary, when system analysis data revealed that gaseous byproducts of high molecular weight and low  $C_p/C_v$  significantly degrade the performance of a laser. Consequently, an  $\text{NF}_3\text{-F}_2$  gas generator was desired which would produce no gases other than  $\text{NF}_3$  and  $\text{F}_2$ . The latter objective can be achieved by a so-called clinker system in which the  $\text{BF}_3$  byproduct is converted by an alkali metal fluoride to a nonvolatile  $\text{BF}_4^-$  salt.



Whereas the feasibility of such a clinker system approach has been well demonstrated, the addition of KF lowers the  $\text{NF}_3\text{-F}_2$  yield per pound of solid propellant and the possibility always exists of having incomplete clinkering.

Realizing these limitations, we have searched during the past year for novel  $\text{NF}_4^+$  salts containing anions that will yield a nonvolatile fluoride, such as  $\text{SnF}_4$  (boiling point = 705 C), after thermal decomposition. No such salts had previously been known, owing to the fact that nonvolatile fluorides are highly polymeric and, therefore, do not behave like strong Lewis acids. This makes the direct synthesis of such salts from  $\text{NF}_3$ ,  $\text{F}_2$ , and the Lewis acid extremely difficult. We found, however, that  $(\text{NF}_4)_2\text{SnF}_6$  can be prepared by the following metathetical reaction in HF solution:



This salt was thoroughly characterized and the results were summarized in manuscript form (see Appendix B).

Further improvements were made by synthesizing novel  $\text{NF}_4^+$  salts derived from  $\text{TiF}_4$  (see Appendix C). Although the usable fluorine content of  $(\text{NF}_4)_2\text{TiF}_6$  (see Table 1) is considerably higher than that of  $(\text{NF}_4)_2\text{SnF}_6$ ,  $\text{TiF}_4$  (sublimation pressure of 760 mm at 284 C) is more volatile than  $\text{SnF}_4$  (b.p. = 705 C) and may require alkali metal fluoride based clinkering.

Table 1: Comparison of the Fluorine Yields of Presently Known  $\text{NF}_3\text{-F}_2$  Gas Generator Systems

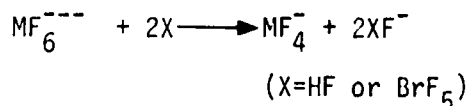
| Rank | System   | Usable F (Weight %) |               |
|------|--|---------------------|---------------|
|      |  | Before              | After Burning |
| 1.   | $(\text{NF}_4)_2\text{NiF}_6$                    | 64.6                | 58.6          |
| 2.   | $(\text{NF}_4)_2\text{TiF}_6^*$                  | 55.6                | 49.6          |
| 3.   | $(\text{NF}_4)_2\text{SnF}_6$                    | 46.0                | 40.0          |
| 4.   | $(\text{NF}_4)_2\text{TiF}_6 \cdot 2.4\text{KF}$ | 39.5                | 33.5          |
| 5.   | $\text{NF}_4\text{BF}_4 \cdot 1.2\text{KF}$      | 38.5                | 32.5          |
| 6.   | $(\text{NF}_4)_2\text{GeF}_6 \cdot 2.4\text{KF}$ | 37.6                | 31.6          |
| 7.   | $\text{NF}_4\text{SnF}_5$                        | 31.3                | 25.3          |
| 8.   | $\text{NF}_4\text{PF}_6 \cdot 1.2\text{KF}$      | 31.2                | 25.2          |
| 9.   | $\text{NF}_4\text{GeF}_5 \cdot 1.2\text{KF}$     | 29.0                | 23.0          |
| 10.  | $\text{NF}_4\text{AsF}_6 \cdot 1.2\text{KF}$     | 27.3                | 21.3          |
| 11.  | $\text{NF}_4\text{SbF}_6 \cdot 1.2\text{KF}$     | 24.0                | 18.0          |
| 12.  | $\text{NF}_4\text{BiF}_6 \cdot 1.2\text{KF}$     | 19.7                | 13.7          |

\*  $(\text{NF}_4)_2\text{TiF}_6$  might require clinkering with KF which would drop its fluorine yield below that of  $(\text{NF}_4)_2\text{SnF}_6$ .

The usable fluorine content was further increased by synthesizing a  $\text{NF}_4^+$  salt of an oxidizing anion. This salt is  $(\text{NF}_4)_2\text{NiF}_6$  (see Appendix D). It has the advantages of containing a doubly charged anion which is "self-clinkering", and an oxidizing anion, thus boosting its usable fluorine content to 64.6 weight % (see Table 1). However, its thermal stability is marginal (see Appendix D), which may limit its potential applications.

Since all of the top ranked  $\text{NF}_4^+$  salts are prepared by metathetical processes, this process was studied in more detail and was significantly improved (see Appendix G). A major breakthrough in the process development was achieved by demonstrating that essentially pure  $\text{NF}_4\text{BF}_4$  can be produced by metathesis. Furthermore, the synthesis of the  $\text{NF}_4\text{SbF}_6$  starting material was improved (see Appendices A and G) and a novel alternate starting material, i.e.  $\text{NF}_4\text{BiF}_6$ , was synthesized and characterized (see Appendix A).

Extensive efforts were undertaken to prepare other novel  $\text{NF}_4^+$  salts. Desired compounds included  $(\text{NF}_4)_3\text{AlF}_6$ ,  $(\text{NF}_4)_3\text{CoF}_6$ ,  $(\text{NF}_4)_3\text{FeF}_6$ ,  $(\text{NF}_4)_3\text{MnF}_6$ ,  $\text{NF}_4\text{AlF}_4$  and  $(\text{NF}_4)_2\text{ZrF}_6$ . Metatheses in either HF or  $\text{BrF}_5$  solution were chosen as synthetic approaches. Unfortunately, efforts along these lines were frustrating owing to the low solubilities of the starting materials in these solvents and solvolysis of the triply charged anions according to:



Efforts to prepare these compounds are being continued and will be summarized in a future report.

In collaboration with Dr. I. Goldberg of Rockwell International's Science Center (who also has an ONR Contract), a joint esr study was carried out to identify some of the intermediates in the uv-photolytic  $\text{NF}_4^+$  salt process. For the  $\text{NF}_3\text{-F}_2\text{-BF}_3$  system, the formation of the novel  $\text{BF}_4$  radical was established. This radical is a key intermediate in the mechanism previously proposed by us

(Ref. 9). A summary of this work will be given in manuscript form in next year's report.

In collaboration with Dr. C. Christenson of Dow Chemical, the ESCA spectra of  $\text{NF}_4^+$  and related salts are being studied. Preliminary results for  $\text{NF}_4\text{BF}_4$  are summarized in Table 2. A comparison with data previously reported by Rosolovskii (Ref. 10) shows that the latter values are indeed much too high.

With the exception of  $\text{NF}_4\text{BF}_4$ , no thermodynamic data are presently available for  $\text{NF}_4^+$  salts. These data are badly needed for performance calculations. A collaborative effort with Prof. R. Peacock of the University of Leicester, England, has been established to acquire such data.

Following the suggestion of Dr. R. Miller, the contract Scientific Officer, the usefulness of solid propellant  $\text{NF}_3\text{-F}_2$  gas generators for the rapid destruction of films or magnetic tapes was demonstrated (see Appendix H).

In summary, the following major breakthroughs in  $\text{NF}_4^+$  chemistry were achieved during the past year:

1. Reduction to practice of the "self-clinkering" concept of  $\text{NF}_4^+$  salts
2. The use of doubly charged anions
3. The use of energetic anions, such as  $\text{NiF}_6^{--}$
4. The synthesis and characterization of the novel  $(\text{NF}_4)_2\text{NiF}_6$ ,  $(\text{NF}_4)_2\text{SnF}_6$ ,  $(\text{NF}_4)_2\text{TiF}_6$  and  $\text{NF}_4\text{BiF}_6$  salts
5. The synthesis of high purity  $\text{NF}_4\text{BF}_4$  by metathesis
6. The identification of the novel  $\text{BF}_4$  radical as a key intermediate in the photolytic formation of  $\text{NF}_4\text{BF}_4$

These results clearly demonstrate the importance and usefulness of the work done under this contract.

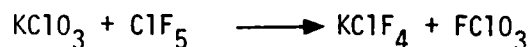
Table 2: ESCA Data for  $\text{NF}_4\text{BF}_4$

|                           | $\text{NF}_4\text{BF}_4$ | CHRISTENSON, CHRISTE<br>(1976) | ROSOLOVSKII ET AL<br>(1972) |
|---------------------------|--------------------------|--------------------------------|-----------------------------|
| BINDING<br>ENERGY<br>(eV) | N1s                      | 413.5                          | (417.3)                     |
|                           | F1s( $\text{NF}_4^+$ )   | 691.3                          | (694.4)                     |
|                           | F1s( $\text{BF}_4^-$ )   | 688.9                          |                             |
|                           | B1s                      | 192.9                          | (195.4)                     |
| BINDING ENERGY            | $\text{NH}_3(\text{s})$  |                                |                             |
|                           | $\text{NH}_4^+$          | 402                            |                             |
|                           | $\text{NO}_2^-$          | 404                            |                             |
|                           |                          | $\text{NO}_3^-$                | 407.2                       |
|                           |                          |                                | $\text{NF}_4^+$             |
|                           |                          |                                | 413.5                       |



## HALOGEN FLUORIDES

Recently, Bougon reported (Ref. 11) the synthesis of the novel  $\text{BrF}_4\text{O}^-$  anion from  $\text{BrO}_3^-$  and  $\text{BrF}_5$ . We have studied the analogous reaction of  $\text{ClO}_3^-$  with  $\text{ClF}_5$  as a possible route to  $\text{ClF}_4\text{O}^-$ . If possible, this reaction would provide a new convenient synthesis for  $\text{ClF}_3\text{O}$ . However instead of the desired  $\text{ClF}_4\text{O}^-$ , the following quantitative reaction occurred:



Attempts were also undertaken to prepare the yet unknown  $\text{BrF}_4\text{O}_2^-$  anion from  $\text{BrO}_4^-$  and  $\text{BrF}_5$ . However instead of  $\text{BrF}_4\text{O}_2^-$ , only the known  $\text{BrF}_4\text{O}^-$  anion was formed in high yield. Good vibrational spectra were obtained for  $\text{BrF}_4\text{O}^-$  and a normal coordinate analysis of this anion is under progress. The results will be given in next year's report in manuscript form. Attempts to record the Raman spectrum of  $\text{CsBrF}_4\text{O}$  in HF solution resulted in a displacement reaction accompanied by  $\text{BrF}_3\text{O}$  formation.

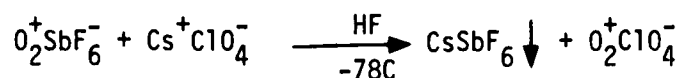
In collaboration with Dr. Goldberg of Rockwell's Science Center, attempts were undertaken to prepare the novel  $\text{ClF}_4\text{O}^\cdot$  radical by  $\gamma$ -irradiation of  $\text{ClF}_3\text{O}$  in an  $\text{SF}_6$  matrix at  $-196^\circ\text{C}$ . However, no esr signals attributable to  $\text{ClF}_4\text{O}^\cdot$  could be detected. Control experiments with  $\text{BrF}_5$  in  $\text{SF}_6$  matrix resulted in the well characterized (Ref. 12, 13)  $\text{BrF}_6^\cdot$  radical.

## SULFUR COMPOUNDS

Normal coordinate analyses of  $\text{SF}_5\text{Br}$  (see Appendix E) and  $\text{SF}_4\text{O}$  (see Appendix F) were carried out. The former is an important starting material for energetic fluorocarbons, and the latter is of interest as a model compound for trigonal bipyramidal halogen compounds. Our results for  $\text{SF}_5\text{Br}$  are in good agreement with those of an independent study recently published by Smardzewski and coworkers (Ref. 14).

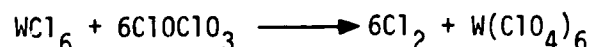
## PERCHLORATES

Attempts were made to synthesize the novel  $O_2^+ClO_4^-$  salt by metathesis in anhydrous HF according to:

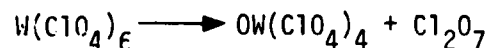


Although the expected  $CsSbF_6$  precipitate was formed, spontaneous decomposition of  $O_2^+ClO_4^-$  with strong gas evolution occurred. This indicates that  $O_2^+ClO_4^-$  is unstable under these conditions. This compound would have been extremely interesting due to its very high oxygen content (73 weight %).

Anhydrous metal perchlorates are of interest as ingredients in explosives and as burning rate modifiers for solid propellants. The reaction of  $WF_6$  with chlorine perchlorate was carried out to examine whether all six chlorines on tungsten could be replaced by perchlorate groups. A long term reaction at  $-45^\circ C$  showed that six equivalents of  $Cl_2$  were formed as expected for the reaction:

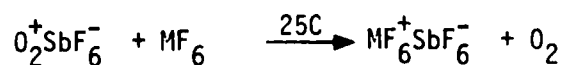


However, some  $Cl_2O_7$  was also present indicating that the following decomposition had occurred:



## TRANSITION METAL FLUORIDES

The interaction of  $O_2^+$  salts with  $WF_6$  and  $MoF_6$  was studied to check whether novel cations can be prepared according to:



However, no interaction was observed in either case.

#### MICROWAVE STUDY OF $O_2F$

The  $O_2F$  radical is of great interest for chemical lasers. Since work in our laboratory had indicated that this radical possesses appreciable stability at room temperature, a structural study of the  $O_2F$  radical in the gas phase appeared feasible. Consequently, contact has been established with Prof. Godfrey of the Monash University in Melbourne, Australia, who will study the  $O_2F^{\cdot}$  radical by microwave spectroscopy. A sample of  $O_2AsF_6$  was prepared by us and will be subjected at Monash to slow vacuum pyrolysis for the  $O_2F$  generation.

#### OXONIUM SALTS

The stable  $OH_3^+$  salts, discovered recently under this contract, are of interest as polymerization catalysts. A sample of  $OH_3^+SbF_6^-$  was prepared and tested at Ciba-Geigy for the polymerization of epoxy resins. The compound was found to be too powerful for commercial applications, resulting in spontaneous polymerization with high heat release. For practical purposes, salts of weaker Lewis acids would have to be prepared and tested.

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Contribution from Rocketdyne, A Division of  
Rockwell International, Canoga Park, California 91304

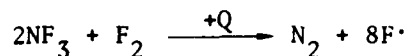
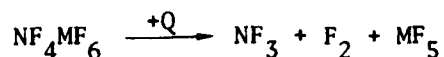
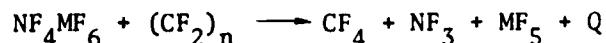
On the Synthesis and Characterization of  $\text{NF}_4\text{BiF}_6$   
and Some Properties of  $\text{NF}_4\text{SbF}_6$

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Introduction

Perfluoroammonium salts are known<sup>1</sup> of the following anions:  $\text{PF}_6^-$ ,  $\text{AsF}_6^-$ ,  $\text{SbF}_6^-$ ,  $\text{SbF}_6 \cdot n\text{SbF}_5^-$ ,  $\text{BF}_4^-$ ,  $\text{GeF}_5^-$ , and  $\text{GeF}_6^{--}$ . Very recently, the synthesis and chemistry of  $\text{NF}_4^+$  salts have received considerable attention owing to their potential for solid propellant  $\text{NF}_3\text{-F}_2$  gas generators for chemical DF lasers. The concept of such a gas generator was conceived<sup>2</sup> and to a large extent developed at Rocketdyne. Originally, the fluorine gas generators were aimed at the direct generation of F atoms by burning a highly overoxidized grain, consisting mainly of an  $\text{NF}_4^+$  salt, with a small amount of fuel, such as Teflon powder, according to:



The heat of reaction (Q) generated in such a system is sufficient to pyrolyze the remaining  $\text{NF}_4\text{MF}_6$  and to dissociate most of the  $\text{NF}_3$  and  $\text{F}_2$  to F atoms. For an  $\text{NF}_3$ - $\text{F}_2$  gas generator, the underlying principle is quite similar, except for keeping the burning temperature lower since dissociation of  $\text{NF}_3$  and  $\text{F}_2$  to F atoms is not required.

In view of the above developments, we were interested in the synthesis of new  $\text{NF}_4^+$  salts and in the characterization of new and known  $\text{NF}_4^+$  salts. In this paper, we report on the synthesis of the new salt  $\text{NF}_4\text{BiF}_6$  and on some properties of the known  $\text{NF}_4\text{SbF}_6$ . Since these two salts can be readily prepared in high yields, they are important starting materials for the syntheses of other  $\text{NF}_4^+$  salts used in  $\text{NF}_3$ - $\text{F}_2$  gas generator compositions.

### Experimental

Materials and Apparatus. The equipment and handling procedures used in this work were identical to those<sup>1</sup> recently described. The  $\text{NF}_4\text{BF}_4$  starting material was prepared by low-temperature uv-photolysis<sup>1</sup> and did not contain any detectable impurities. The  $\alpha$ - $\text{BiF}_5$  was purchased from Ozark Mahoning Co. and did not contain any impurities detectable by Raman spectroscopy. The  $\text{NF}_4\text{Sb}_2\text{F}_{11}$  was prepared as described.<sup>3</sup>

Synthesis of  $\text{NF}_4\text{BiF}_6$  by Displacement Reaction without Solvent. Pure  $\text{NF}_4\text{BF}_4$  (10.1 mmol) and  $\alpha$ - $\text{BiF}_5$  (10.1 mmol) were powdered, mixed, and placed in a prepassivated (with  $\text{ClF}_3$ ) 95 ml Monel cylinder. The cylinder was heated to  $180^\circ$  for 1.5 h. Products, volatile at  $20^\circ$ , were removed by pumping and separated by fractional condensation. They consisted of 7.8 mmol of  $\text{BF}_3$  in addition to a small amount of material noncondensable at  $-196^\circ$ . The amount of  $\text{BF}_3$  evolution was confirmed by the weight loss of the solid containing cylinder. The conversion of  $\text{NF}_4\text{BF}_4$  to  $\text{NF}_4\text{BiF}_6$  was further confirmed

by Raman spectroscopy of the solid. The solid was removed from the cylinder, finely powdered, returned to the cylinder, and heated to 175° for an additional 18 hours. This resulted in the evolution of an additional 2.3 mmol of  $\text{BF}_3$ , in excellent agreement with the observed weight loss. The complete conversion of  $\text{NF}_4\text{BF}_4$  to  $\text{NF}_4\text{BiF}_6$  was confirmed by infrared and Raman spectroscopy and elemental analysis. Anal. Calcd for  $\text{NF}_4\text{BiF}_6$ :  $\text{NF}_3$ , 17.15;  $\text{BiF}_3$ , 64.49. Found:  $\text{NF}_3$ , 16.9;  $\text{BiF}_3$ , 60.0. An explanation for the low  $\text{BiF}_3$  value is given below.

Synthesis of  $\text{NF}_4\text{BiF}_6$  by Displacement Reaction in HF. Dry HF (5 ml liquid) was added at -78° to a Teflon FEP ampoule containing  $\text{NF}_4\text{BF}_4$  and  $\text{BiF}_5$  (9.9 mmol of each). The mixture was agitated at 20° for several hours and gas evolution was observed. The volatile products were pumped off at 20° and the HF treatment was repeated. After removal of the volatile products from the second HF treatment, 4.075 g of a white, stable solid (weight calculated for 9.9 mmol of  $\text{NF}_4\text{BiF}_6$  = 4.089 g) was left behind which was shown by infrared and Raman spectroscopy to be identical to the analyzed product obtained from the above described thermal displacement reaction.

Direct Synthesis of  $\text{NF}_4\text{BiF}_6 \cdot n\text{BiF}_5$ . In a typical experiment, a mixture of  $\text{NF}_3$  (238 mmol),  $\text{F}_2$  (238 mmol), and  $\text{BiF}_5$  (10.06 mmol) in a prepassivated 95 ml Monel cylinder was heated for 30 hours to 175° under an autogenous pressure of 167 atm. Unreacted  $\text{NF}_3$  and  $\text{F}_2$  (~463 mmol total) were pumped off at 20° leaving behind 3.75 g of a white, stable solid (weight calcd for 6.29 mmol of  $\text{NF}_4\text{BiF}_6 \cdot 0.6\text{BiF}_5$  = 3.745 g). Anal. Calcd for  $\text{NF}_4\text{BiF}_6 \cdot 0.6\text{BiF}_5$ :  $\text{NF}_3$ , 11.92;  $\text{BiF}_3$ , 71.60. Found:  $\text{NF}_3$ , 11.9;  $\text{BiF}_3$ , 69.00.

Pyrolysis of  $\text{NF}_4\text{BiF}_6 \cdot n\text{BiF}_5$ . A sample (3.29 mmol) of  $\text{NF}_4\text{BiF}_6 \cdot 1.46\text{BiF}_5$ , prepared as described above except for using a significantly shorter reaction time, was subjected to vacuum pyrolysis at 280° for 1.5 hours. The white crystalline residue (1.13 g) was identified by vibrational spectroscopy and its x-ray diffraction powder pattern to be mainly  $\text{NF}_4\text{BiF}_6$  (weight calcd for 3.29 mmol of  $\text{NF}_4\text{BiF}_6$  = 1.36 g) corresponding to a yield of 83%.

Synthesis of  $\text{NF}_4\text{SbF}_6$ . The thermal reaction<sup>4</sup> of  $\text{NF}_3\text{-F}_2\text{-SbF}_5$  at  $115^\circ$ , followed by vacuum pyrolysis at  $200^\circ$ , produces<sup>3</sup> a product of the approximate composition  $\text{NF}_4\text{Sb}_2\text{F}_{11}$ . This product can be converted to  $\text{NF}_4\text{SbF}_6$  by vacuum pyrolysis at higher temperature, however, this  $\text{SbF}_5$  removal is accompanied by a competing reaction, i.e. the thermal decomposition of some of the desired  $\text{NF}_4\text{SbF}_6$ . Pyrolysis at  $250\text{-}260^\circ$  for 1 to 1.5 hours in a dynamic vacuum resulted in complete conversion to  $\text{NF}_4\text{SbF}_6$ . Measurement of the  $\text{NF}_3$  evolved during this pyrolysis showed that less than 3% of the  $\text{NF}_4\text{SbF}_6$  had undergone decomposition. When the pyrolysis was carried out at  $275\text{-}300^\circ$ , even for relatively short periods of time, significantly higher losses of  $\text{NF}_4\text{SbF}_6$  due to thermal decomposition occurred.

In a typical experiment,  $\text{NF}_4\text{Sb}_2\text{F}_{11}$  (31.0 mmol) in a 95 ml Monel cylinder was pyrolyzed in a dynamic vacuum at  $255^\circ$  for 80 min. The evolved  $\text{SbF}_5$  was condensed in a Teflon-FEP U-trap kept at  $-196^\circ$ . The white solid residue consisted of 30.4 mmol of  $\text{NF}_4\text{SbF}_6$  (98 mole % yield based on  $\text{NF}_4^+$ ). Anal. Calcd for  $\text{NF}_4\text{SbF}_6$ :  $\text{NF}_3$ , 21.80; Sb, 37.38. Found:  $\text{NF}_3$ , 21.72; Sb, 37.41; Ni, 0.08; Cu, 0.03.

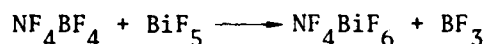
Elemental Analyses. For the elemental analyses, a weighed amount (several mmol) of the  $\text{NF}_4^+$  salt was placed in the bottom of a Teflon-FEP U-trap, which was closed off by valves. The trap was cooled to  $-196^\circ$  and several ml of distilled water was frozen out in the upper section of the U-trap. The frozen water was shaken down into the cold bottom section of the U-tube and the ice and the  $\text{NF}_4^+$  salt were mixed while being cold. This mixing procedure was found important to avoid violent reactions between solid  $\text{NF}_4^+$  salts and isolated droplets of liquid water, which sometimes were encountered when thawing the ice in the upper part of the tube and allowing the liquid water to run down onto the  $\text{NF}_4^+$  salt. The mixture of ice and  $\text{NF}_4^+$  salt was warmed to  $20^\circ$  for 30 min. Upon melting of the ice, gas evolution occurred. The contents of the trap were cooled and the evolved  $\text{O}_2$  and  $\text{NF}_3$  were distilled off at  $-196^\circ$  and  $-126^\circ$ , respectively, and were measured volumetrically. For  $\text{NF}_4\text{SbF}_6$ , the aqueous hydrolysate was analyzed for Sb by x-ray fluorescence spectroscopy. For the  $\text{BiF}_5$  salts, a white, water-insoluble precipitate



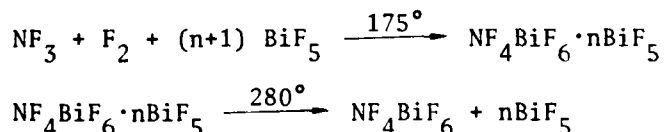
formed on hydrolysis. This precipitate was filtered off at 0°, washed with a small amount of cold distilled water, dried at 103°, and weighed. It was identified by its x-ray powder diffraction pattern<sup>4</sup> and by electron microprobe x-ray analysis as BiF<sub>3</sub>. Anal. Calcd for BiF<sub>3</sub>: Bi, 78.57; F, 21.43; O, 0. Found: Bi, 78.6; F, 21.3; O, 0. Although 93 to 97% of the BiF<sub>3</sub> could be isolated in this manner, the solubility of BiF<sub>3</sub>, particularly in the presence of HF, is not low enough<sup>5</sup> to permit a quantitative precipitation of BiF<sub>3</sub>.

### Results and Discussion

Syntheses. The new NF<sub>4</sub><sup>+</sup> salt NF<sub>4</sub>BiF<sub>6</sub> was prepared either from NF<sub>4</sub>BF<sub>4</sub> and BiF<sub>5</sub> by the following displacement reaction



or directly by the elevated temperature-pressure method<sup>6</sup> followed by vacuum pyrolysis



The displacement reaction can be carried out either at 25° in HF solution or in the absence of a solvent at elevated temperature.

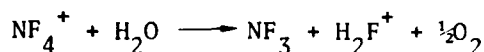
The synthesis of NF<sub>4</sub>BiF<sub>6</sub> is more difficult than that of NF<sub>4</sub>SbF<sub>6</sub> owing to the fact that at ambient temperature α-BiF<sub>5</sub> is a nonvolatile, polymeric, trans-fluorine bridged solid. Consequently, temperatures above the melting point (151.4°) of BiF<sub>5</sub> are required for both the displacement reaction and the elevated temperature-pressure method. Since removal of excess BiF<sub>5</sub> is inconvenient, the displacement reactions are best carried out with stoichiometric amounts of starting materials. As for SbF<sub>5</sub>,<sup>6</sup> the direct synthesis of the NF<sub>4</sub><sup>+</sup> perfluorobismuthate salt at elevated temperature and pressure tends to produce polyanions (mainly Bi<sub>2</sub>F<sub>11</sub><sup>-</sup>).<sup>7</sup> The feasibility of converting these salts to NF<sub>4</sub>BiF<sub>6</sub> by vacuum pyrolysis was demonstrated, but no effort was made to maximize the reaction conditions.

The pyrolysis of  $\text{NF}_4\text{Sb}_2\text{F}_{11}$  to  $\text{NF}_4\text{SbF}_6$  and  $\text{SbF}_5$  was briefly investigated, when we discovered that the reaction conditions ( $200^\circ$ ) previously recommended<sup>8</sup> for the pyrolysis were not suitable for obtaining pure  $\text{NF}_4\text{SbF}_6$ . In our experience, a significantly higher pyrolysis temperature of about  $250^\circ$  was required for the production of essentially pure  $\text{NF}_4\text{SbF}_6$ . At this temperature, little or no decomposition of the  $\text{NF}_4\text{SbF}_6$  itself took place. Based on the results obtained in our laboratory, the thermal reaction between approximately equimolar amounts of  $\text{NF}_3$ ,  $\text{F}_2$ , and  $\text{SbF}_5$  at temperatures ranging from  $115$  to  $200^\circ$  and autogenous pressures of about 200 atm produces a product of the composition  $\text{NF}_4\text{SbF}_6 \cdot n\text{SbF}_5$  with  $n$  ranging from 2.1 to 3.2 depending on the exact reaction conditions. Vacuum pyrolysis of these products at  $200^\circ$  reduces  $n$  to a level ranging from 0.8 to 1.1. Pyrolysis at  $260^\circ$  reduces the value of  $n$  to zero.

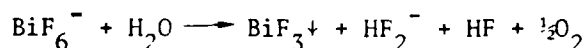
Properties. The composition of the  $\text{NF}_4^+$  salts was established by both the observed material balances and elemental analyses. The  $\text{NF}_4\text{BiF}_6$  salt is a white crystalline solid melting in a sealed glass capillary at about  $341^\circ$ . The x-ray powder diffraction pattern of the sample prepared by pyrolysis of  $\text{NF}_4\text{BiF}_5 \cdot n\text{BiF}_5$  is given as supplementary material. It could readily be indexed for a tetragonal unit cell, analogous to those of  $\text{NF}_4\text{PF}_6$ ,<sup>1</sup>  $\text{NF}_4\text{AsF}_6$ ,<sup>9</sup> and  $\text{NF}_4\text{SbF}_6$  (see Table I). Several weak lines were of variable intensity could not be indexed for a tetragonal unit cell, and corresponding lines had not been observed for the other isotypic  $\text{NF}_4\text{MF}_6$  salts. Consequently, these extra lines are attributed to impurities, such as polyanion salts, and have not been included in the listing.

The  $\text{NF}_4\text{SbF}_6$  salts melts at about  $318^\circ$ . Its x-ray powder diffraction pattern is given as supplementary material. All the observed lines could be indexed for a tetragonal unit cell, analogous to those observed for the other  $\text{NF}_4\text{MF}_6$  salts (see Table I). As expected, the unit cell dimensions and calculated densities increase in the order:  $\text{PF}_6^- < \text{AsF}_6^- < \text{SbF}_6^- < \text{BiF}_6^-$ .

The hydrolyses of  $\text{NF}_4\text{SbF}_6$  and  $\text{NF}_4\text{BiF}_6$  showed a distinct difference as far as the amount of oxygen evolution is concerned. The  $\text{NF}_4\text{SbF}_6$  behaved like the previously studied<sup>1</sup>  $\text{NF}_4^+$  salts and generated  $\text{O}_2$  according to:

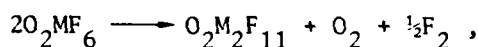


This reaction, however, is not quantitative owing to a competing reaction<sup>1</sup> involving the formation of some  $\text{H}_2\text{O}_2$ . Thus, for  $\text{NF}_4\text{SbF}_6$ , only 0.45 mol of  $\text{O}_2$  was observed per mol of  $\text{NF}_3$ . For  $\text{NF}_4\text{BiF}_6$ , however, 0.86 mol of  $\text{O}_2$  was obtained per mol of  $\text{NF}_3$ . Furthermore, no evidence for the formation of brown  $\text{Bi}_2\text{O}_5$  (generated when  $\text{BiF}_5$  is hydrolyzed) was observed, but white  $\text{BiF}_3$  was precipitated. This oxidation of  $\text{H}_2\text{O}$  by  $\text{BiF}_6^-$  according to



can account for the additional  $\text{O}_2$  evolution, which by analogy<sup>1</sup> with  $\text{NF}_4^+$  might not be quantitative owing to the formation of some  $\text{H}_2\text{O}_2$ .

The oxygen evolution during the hydrolysis of the closely related  $\text{O}_2^+$  salts has recently been studied.<sup>10</sup> In agreement with our findings for  $\text{NF}_4^+$  salts, the observed  $\text{O}_2$  evolution was generally lower than the calculated values. However, for  $\text{O}_2\text{BiF}_6$ , no evidence for the reduction of pentavalent bismuth was reported. Furthermore, the given explanation, i.e. that the low observed  $\text{O}_2$  values are due to samples which had undergone partial decomposition according to



cannot account for the low  $\text{O}_2$  value found for salts, such as  $\text{O}_2\text{AsF}_6$ , which contain a volatile Lewis acid and do not form a stable  $\text{M}_2\text{F}_{11}^-$  anion. Therefore, some of the conclusions, such as "all dioxygenyl salts prepared so far are intrinsically unstable at room temperature", which are based on the low observed oxygen values, are open to question. Obviously, competing side reactions, such as those observed for the  $\text{NF}_4^+$  salts, might play an important role and give rise to low oxygen values.

Vibrational Spectra. The vibrational spectra of  $\text{NF}_4\text{BiF}_6$ ,  $\text{NF}_4\text{BiF}_6 \cdot 0.6\text{BiF}_5$ , and  $\text{NF}_4\text{SbF}_6$  are shown in Figure 1. The observed frequencies and their assignments are summarized in Table II. The spectra are in excellent agreement with those previously reported for the  $\text{NF}_4^+$  cation<sup>1</sup> and the  $\text{BiF}_6^{-7,11,12}$  and  $\text{SbF}_6^{-7,12-15}$  anions, thus confirming the ionic nature of these adducts. By analogy with the previously studied<sup>1</sup>  $\text{NF}_4^+$  salts, the degeneracy of some of the modes is lifted and crystal field splittings are observed. For example, the antisymmetric  $\text{NF}_4^+$  stretching mode  $\nu_3(\text{F}_2)$  is split into three components, and the  $\nu_3(\text{F}_{1u})$  and the  $\nu_2(\text{E}_g)$  mode of  $\text{SbF}_6^-$  show a splitting into three and two components, respectively. The presence of polyanions, such as  $\text{Bi}_2\text{F}_{11}^-$ ,<sup>7</sup> in the  $\text{NF}_4\text{BiF}_6 \cdot n\text{BiF}_5$  adducts is apparent from the appearance of a medium intense infrared band at  $452\text{ cm}^{-1}$ , which is attributed to the stretching mode of the Bi-F-Bi bridge. Furthermore, additional bands were observed in the region of the BiF stretching and deformation modes. The maximum of the most intense BiF stretching infrared band was found to vary somewhat from sample to sample and varied from  $575$  to  $605\text{ cm}^{-1}$ . In addition, some of the pyrolysis products showed weak infrared bands at  $475$  and  $400\text{ cm}^{-1}$ . A comparison of the spectra of  $\text{NF}_4\text{BiF}_6$  and  $\text{NF}_4\text{BiF}_6 \cdot n\text{BiF}_5$  with those of  $\text{NF}_4\text{SbF}_6$  and  $\text{NF}_4\text{Sb}_2\text{F}_{11}^1$  shows a similar pattern for both when going from  $\text{MF}_6^-$  to  $\text{M}_2\text{F}_{11}^-$ .

Summary. The new  $\text{NF}_4^+$  salt  $\text{NF}_4\text{BiF}_6$  was prepared by the reaction between equimolar amounts of  $\text{NF}_4\text{BF}_4$  and  $\text{BiF}_5$  either at  $180^\circ$  without solvent or at  $20^\circ$  in  $\text{Hf}$  solution. A salt of the composition  $\text{NF}_4\text{BiF}_6 \cdot n\text{BiF}_5$  ( $n=0.6$  to  $1.5$ ) was prepared directly from  $\text{NF}_3$ ,  $\text{F}_2$ , and  $\text{BiF}_5$  at elevated temperature and pressure. It was converted to  $\text{NF}_4\text{BiF}_6$  by vacuum pyrolysis at  $280^\circ$ . The salts were characterized by elemental analyses and vibrational spectroscopy, and their hydrolyses were studied. The pyrolysis of  $\text{NF}_4\text{SbF}_6 \cdot n\text{SbF}_5$  to  $\text{NF}_4\text{SbF}_6$  was briefly investigated, and the vibrational spectrum and x-ray powder pattern of  $\text{NF}_4\text{SbF}_6$  are reported.

Acknowledgement. We are indebted to Dr. L. R. Grant for helpful discussions and to the Office of Naval Research for financial support.

Supplementary Material Available. Listings of the observed x-ray powder diffraction patterns of  $\text{NF}_4\text{BiF}_6$  and  $\text{NF}_4\text{SbF}_6$  (2 pages). Ordering information is given on any current masthead page.

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Table 1. Crystallographic Data of  $\text{NF}_4\text{SbF}_6$  and  $\text{NF}_4\text{BiF}_6$   
Compared to Those of  $\text{NF}_4\text{PF}_6$  and  $\text{NF}_4\text{AsF}_6$

|                             | Tetragonal Unit Cell Dimensions |                   |                     | Z | Volume ( $\text{\AA}^3$ )<br>per F | Calcd Density<br>( $\text{g/cm}^3$ ) |
|-----------------------------|---------------------------------|-------------------|---------------------|---|------------------------------------|--------------------------------------|
|                             | a( $\text{\AA}$ )               | c( $\text{\AA}$ ) | V( $\text{\AA}^3$ ) |   |                                    |                                      |
| $\text{NF}_4\text{PF}_6^a$  | 7.577                           | 5.653             | 324.53              | 2 | 16.23                              | 2.41                                 |
| $\text{NF}_4\text{AsF}_6^b$ | 7.70                            | 5.73              | 339.73              | 2 | 16.99                              | 2.72                                 |
| $\text{NF}_4\text{SbF}_6$   | 7.903                           | 5.806             | 362.63              | 2 | 18.13                              | 2.98                                 |
| $\text{NF}_4\text{BiF}_6$   | 8.006                           | 5.821             | 373.10              | 2 | 18.66                              | 3.68                                 |

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(a) Ref. 1

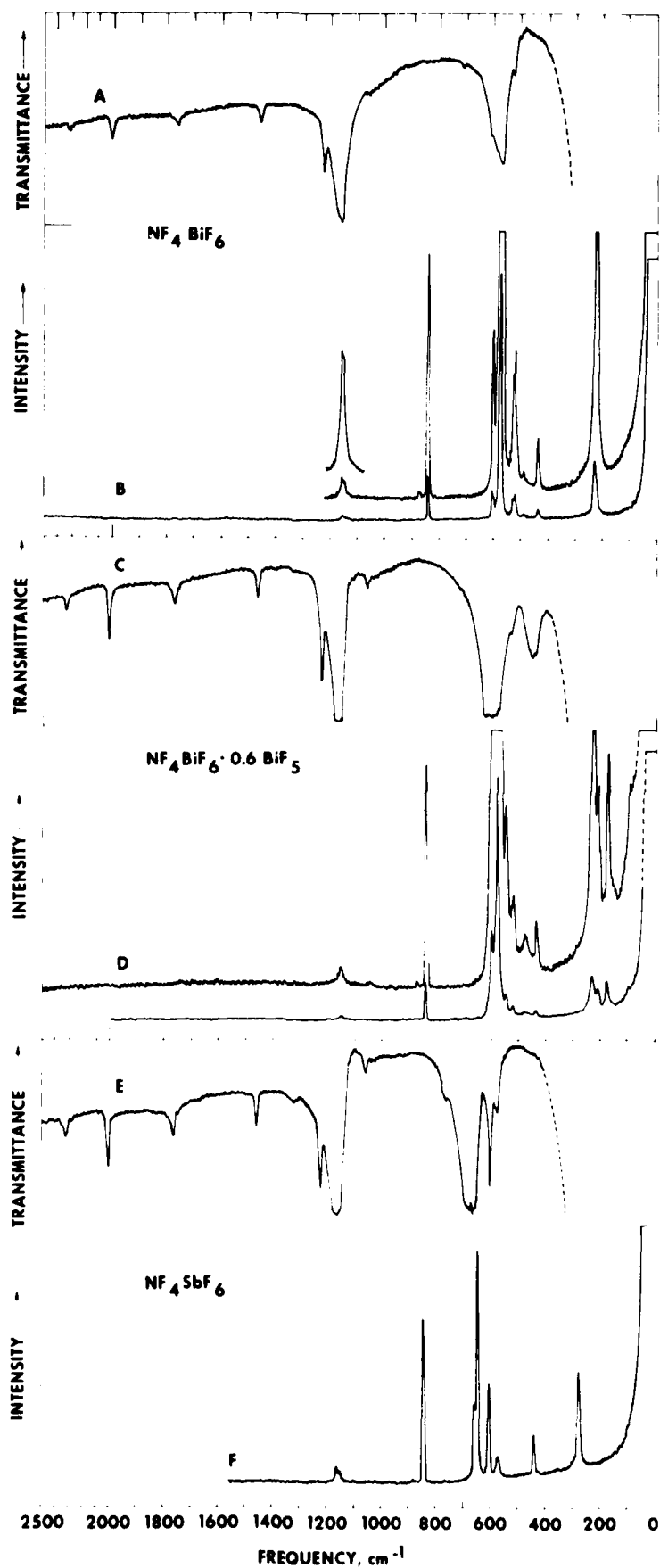
(b) Ref. 7



Diagram Caption

Figure 1. Vibrational Spectra of  $\text{NF}_4\text{BiF}_6$ ,  $\text{NF}_4\text{BiF}_6 \cdot 0.6\text{BiF}_5$ , and  $\text{NF}_4\text{SbF}_6$ .  
Traces A, C, and E: Infrared spectra of the solids in silver chloride disks; the absorptions below  $300\text{ cm}^{-1}$  (broken lines) are due to the AgCl windows. Traces B, D, and F: Raman spectra of the solids recorded at different sensitivities; the spectral slit width used at the lower sensitivity levels was  $2\text{ cm}^{-1}$ .





R-77-112

A-13

Supplementary Material:

"On the Synthesis and Characterization of  $\text{NF}_4\text{BiF}_6$  and Some Properties of  $\text{NF}_4\text{SbF}_6$ ",  
by K. O. Christe, R. D. Wilson, and C. J. Schack.

Table 3. X-Ray Powder Data for  $\text{NF}_4\text{BiF}_6$ <sup>a</sup>

| d obsd | d calcd | Int   | h | k | l |
|--------|---------|-------|---|---|---|
| 5.62   | 5.66    | s     | 1 | 1 | 0 |
| 4.67   | 4.71    | mw    | 1 | 0 | 1 |
| 4.09   | 4.06    | w     | 1 | 1 | 1 |
| 4.00   | 4.00    | vs    | 2 | 0 | 0 |
| 3.30   | 3.30    | mw    | 2 | 0 | 1 |
| 3.05   | 3.05    | mw    | 2 | 1 | 1 |
| 2.832  | 2.831   | mw    | 2 | 2 | 0 |
| 2.735  | 2.735   | mw    | 1 | 0 | 2 |
| 2.589  | 2.588   | w     | 1 | 1 | 2 |
| 2.547  | 2.546   | mw    | 2 | 2 | 1 |
| 2.321  | 2.320   | mw    | 3 | 1 | 1 |
| 2.257  | 2.258   | w     | 2 | 1 | 2 |
| 2.076  | 2.075   | vw    | 3 | 2 | 1 |
| 2.025  | 2.029   | w     | 2 | 2 | 2 |
| 1.889  | 1.889   | mw,br | 4 | 0 | 1 |
|        |         |       | 3 | 3 | 0 |
|        |         |       | 1 | 0 | 3 |
| 1.848  | 1.842   | w     | 4 | 1 | 1 |
| 1.832  | 1.835   | vw    | 1 | 1 | 3 |
| 1.800  | 1.795   | mw    | 3 | 3 | 1 |
| 1.772  | 1.765   | w     | 3 | 2 | 2 |
| 1.706  | 1.706   | w     | 2 | 1 | 3 |

(a) tetragonal,  $a=8.006\text{\AA}$ ,  $c=5.821\text{\AA}$ ,  $\text{Cu K}_\alpha$  radiation  
Ni filter.

Table 4. X-Ray Powder Data for  $\text{NF}_4\text{SbF}_6$  <sup>a</sup>

| d obsd | d calcd | Int    | h | k | l |
|--------|---------|--------|---|---|---|
| 5.55   | 5.59    | s      | 1 | 1 | 0 |
| 4.65   | 4.68    | s      | 1 | 0 | 1 |
| 4.03   | 4.03    | vs, br | { | 1 | 1 |
|        |         |        |   | 0 | 0 |
| 3.27   | 3.27    | mw     | 2 | 0 | 1 |
| 3.014  | 3.018   | s      | 2 | 1 | 1 |
| 2.793  | 2.793   | mw     | 2 | 2 | 0 |
| 2.722  | 2.724   | m      | 1 | 0 | 2 |
| 2.515  | 2.517   | m      | 2 | 2 | 1 |
| 2.296  | 2.295   | m      | 3 | 1 | 1 |
| 2.243  | 2.243   | m      | 2 | 1 | 2 |
| 2.053  | 2.050   | vw     | 3 | 2 | 1 |
| 1.979  | 1.975   | w      | 4 | 0 | 0 |
| 1.953  | 1.950   | m      | 3 | 0 | 2 |
| 1.879  | 1.879   | m      | 1 | 0 | 3 |
| 1.827  | 1.828   | m      | 1 | 1 | 3 |
| 1.775  | 1.773   | mw     | 3 | 3 | 1 |
| 1.757  | 1.757   | m      | { | 4 | 2 |
|        |         |        |   | 2 | 0 |
|        |         |        | { | 3 | 2 |
|        |         |        |   | 2 | 2 |
| 1.699  | 1.697   | ms     | 2 | 1 | 3 |
| 1.600  | 1.599   | w      | 4 | 1 | 2 |
| 1.558  | 1.559   | w      | 3 | 0 | 3 |
| 1.532  | 1.530   | w      | 3 | 1 | 3 |
| 1.505  | 1.509   | w      | 4 | 2 | 2 |
| 1.453  | 1.451   | w      | 0 | 0 | 4 |
| 1.429  | 1.427   | vw     | 1 | 0 | 4 |
| 1.405  | 1.404   | vw     | 1 | 1 | 4 |
| 1.396  | 1.397   | w      | 4 | 4 | 0 |
| 1.366  | 1.366   | w      | 5 | 1 | 2 |

(a) tetragonal,  $a=7.903\text{\AA}$ ,  $c=5.806\text{\AA}$ , Cu  $K_\alpha$  radiation  
Ni filter

Contribution from Rocketdyne, A Division of  
Rockwell International, Canoga Park, California 91304

Synthesis and Characterization of  $(\text{NF}_4)_2\text{SnF}_6$  and  $\text{NF}_4\text{SnF}_5$

Karl O. Christe\*, Carl J. Schack, and Richard D. Wilson

Received 8 April 1976

Abstract

The novel  $\text{NF}_4^+$  salt  $(\text{NF}_4)_2\text{SnF}_6$  was prepared by metathesis between  $\text{Cs}_2\text{SnF}_6$  and  $\text{NF}_4\text{SbF}_6$  in HF solution. It is a white solid, stable to above  $200^\circ$ . Based on its x-ray powder data, it crystallizes in the tetragonal system and is isotypic with  $(\text{NF}_4)_2\text{GeF}_6$ . Its composition was established by elemental analysis, and the presence of tetrahedral  $\text{NF}_4^+$  and octahedral  $\text{SnF}_6^{--}$  ions in the solid state and in  $\text{BrF}_5$  solution was demonstrated by vibrational and  $^{19}\text{F}$  nmr spectroscopy, respectively. The salt  $\text{NF}_4\text{SnF}_5$  was obtained in quantitative yield from the displacement reaction between equimolar amounts of  $\text{NF}_4\text{BF}_4$  and  $\text{SnF}_4$  in HF solution. When a large excess of  $\text{NF}_4\text{BF}_4$  was used, the main product was again  $\text{NF}_4\text{SnF}_5$  and only a small amount of  $(\text{NF}_4)_2\text{SnF}_6$  was formed. The  $\text{NF}_4\text{SnF}_5$  salt was characterized by elemental analysis, vibrational and  $^{19}\text{F}$  nmr spectroscopy, and x-ray powder data. The vibrational spectra of the solid and the  $^{19}\text{F}$  nmr spectra of  $\text{BrF}_5$  solutions show that  $\text{SnF}_5^-$  possesses a polymeric structure of cis-fluorine bridged  $\text{SnF}_6$  octahedra, analogous to that observed for  $\text{GeF}_5^-$  in  $\text{NF}_4\text{GeF}_5$ . The potential of  $(\text{NF}_4)_2\text{SnF}_6$  for a "self-clinkering"  $\text{NF}_3\text{-F}_2$  gas generator is briefly discussed.

Introduction

Perfluoroammonium salts are of significant interest owing to their potential for solid propellant  $\text{NF}_3\text{-F}_2$  gas generators for chemical HF-DF lasers.<sup>1</sup> Salts are known of the following anions:  $\text{PF}_6^-$ ,  $\text{AsF}_6^-$ ,  $\text{SbF}_6^-$ ,  $\text{SbF}_6^- \cdot n\text{SbF}_5$ ,  $\text{BiF}_6^-$ ,

$\text{BiF}_6^- \cdot n\text{BiF}_5$ ,  $\text{BF}_4^-$ ,  $\text{GeF}_5^-$ , and  $\text{GeF}_6^{--}$ .<sup>1,2</sup> All these salts are derived from Lewis acids which are volatile and either completely or at least partially monomeric at temperatures below the thermal decomposition temperature of their  $\text{NF}_4^+$  salts. Since these volatile Lewis acids are undesirable for  $\text{NF}_3$ - $\text{F}_2$  gas generators, they must be removed by complexing (clinker formation) with a strong Lewis base, such as KF. Since the addition of a clinker forming component degrades the performance of an  $\text{NF}_3$ - $\text{F}_2$  gas generator, the synthesis of  $\text{NF}_4^+$  salts, derived from nonvolatile Lewis acids, became very desirable. However, this objective presented a synthetic challenge, since nonvolatile Lewis acids are highly polymeric and already possess favorable high coordination numbers. Consequently, these polymeric compounds are quite unreactive and do not behave like strong Lewis acids, thus rendering a direct synthesis<sup>3</sup> from  $\text{NF}_3$ ,  $\text{F}_2$ , and the Lewis acid impossible. In this paper we report the synthesis of  $\text{NF}_4^+$  salts derived from  $\text{SnF}_4$ , a doubly trans-fluorine bridged polymer<sup>4,5</sup> subliming at  $704^\circ$ , using metathetical<sup>6,7</sup> and displacement<sup>1,2</sup> reactions.

### Experimental

Materials and Apparatus. The equipment and handling procedures used in this work were identical to those recently described.<sup>1,2</sup> The  $\text{NF}_4\text{BF}_4$ <sup>1</sup> and  $\text{NF}_4\text{SbF}_6$ <sup>2</sup> starting materials were prepared as previously reported. The  $\text{SnF}_4$  (Ozark Mahoning) and  $\text{SnCl}_4$  (Baker) were used as received. The  $\text{NF}_3$  and  $\text{F}_2$  were prepared at Rocketdyne, the HF (Matheson) was dried as previously described,<sup>8</sup> and the  $\text{BrF}_5$  (Matheson) was purified by fractional condensation prior to use. The CsF was fused in a platinum crucible and powdered in the dry box.

Synthesis of  $\text{Cs}_2\text{SnF}_6$ . Dry CsF (10.45 mmol) and  $\text{SnCl}_4$  (5.22 mmol) were combined in a passivated Teflon FEP ampoule. Anhydrous HF (10 ml liquid) was added, and the mixture was agitated at  $20^\circ$  for several hours until HCl evolution had ceased and a clear solution was obtained. The volatile materials were pumped off at  $50^\circ$ . The white solid residue (2.604 g, weight calcd for 5.22 mmol of  $\text{Cs}_2\text{SnF}_6$  = 2.600 g) was shown by infrared and Raman spectroscopy<sup>9,10</sup> and its x-ray diffraction powder pattern<sup>11</sup> to be of excellent purity.

If  $\text{SnF}_4$  is readily available, the following synthesis of  $\text{Cs}_2\text{SnF}_6$  was found to be somewhat more convenient. A mixture of  $\text{CsF}$  and  $\text{SnF}_4$  (2:1 mol ratio) was fused in a covered platinum crucible until a clear melt was obtained. Alternately,  $\text{CsF}$  and  $\text{SnF}_4$  (2:1 mol ratio) was agitated in anhydrous  $\text{HF}$  until a clear solution was obtained ( $\text{SnF}_4$  is only very sparingly soluble in  $\text{HF}$ ). In both cases the resulting products were shown by spectroscopic techniques to be undistinguishable from that obtained by the above method.

Synthesis of  $(\text{NF}_4)_2\text{SnF}_6$ . The small-scale metathetical reactions were carried out in the apparatus depicted in Figure 1. It consisted of three Teflon FEP U-traps interconnected by Monel unions (Swagelok) and closed off at both ends by a Monel valve. The union between trap II and trap III contained a Teflon filter (porous Teflon sheet, 1/16" thickness from Russel Assoc. Inc.) and was held in place by a press fit. The passivated apparatus was taken to the dry box and  $\text{Cs}_2\text{SnF}_6$  and  $\text{NF}_4\text{SbF}_6$  (in a 1:2 mole ratio) were placed into traps I and II, respectively. The apparatus was connected to the vacuum line through flexible corrugated Teflon FEP tubing. Anhydrous  $\text{HF}$ , in an amount sufficient to just dissolve the starting materials, was added to traps I and II. Trap I was flexed to allow the  $\text{Cs}_2\text{SnF}_6$  solution to run into trap II containing the  $\text{NF}_4\text{SbF}_6$  solution. Upon contact of the two solutions, copious amounts of a white precipitate ( $\text{CsSbF}_6$ ) formed. The contents of trap II were agitated for several minutes to obtain good mixing. Then the apparatus was inverted to allow the solution to run onto the filter. To generate a pressure differential across the filter, trap III was cooled to  $-80^\circ$ . After completion of the filtration step, trap III was warmed to ambient temperature and the  $\text{HF}$  solvent was pumped off. The solid residue on top of the filter consisted mainly of  $\text{CsSbF}_6$ , whereas the solid collected in trap III was mainly the desired  $(\text{NF}_4)_2\text{SnF}_6$ .

The following example gives a typical product distribution obtainable with the above procedure and apparatus. Starting materials:  $\text{NF}_4\text{SbF}_6$  (9.72 mmol),  $\text{Cs}_2\text{SnF}_6$  (4.86 mmol); weight of solid on filter = 4.24 g; weight of solid in trap III = 1.36 g (weight calcd for 4.86 mmol of  $(\text{NF}_4)_2\text{SnF}_6$  = 2.01 g). Elemental analysis for solid from trap III. Found:  $\text{NF}_3$ , 31.5; Sn, 25.1; Sb, 5.9; Cs, 1.3. Calcd for a mixture (mol %) of 82.8  $(\text{NF}_4)_2\text{SnF}_6$ , 12.9  $\text{NF}_4\text{SbF}_6$ , and 4.3  $\text{CsSbF}_6$ :  $\text{NF}_3$ , 31.72; Sn, 24.60; Sb, 5.24; Cs, 1.43.

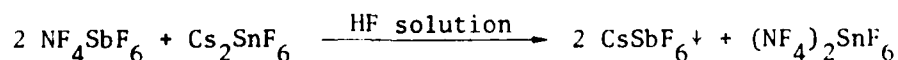
Synthesis of  $\text{NF}_4\text{SnF}_5$ . A mixture of  $\text{NF}_4\text{BF}_4$  and  $\text{SnF}_4$  (9.82 mmol each) was placed into a passivated Teflon-FEP ampoule containing a Teflon coated magnetic stirring bar. Anhydrous HF (10 ml liquid) was added at  $-78^\circ$ , and the resulting suspension was stirred at  $25^\circ$  for 2 hours. The volatile material was pumped off at  $35^\circ$  leaving behind a white stable solid which, on the basis of its weight (3.094 g) and Raman spectrum, consisted of 83 mol percent  $\text{NF}_4\text{SnF}_5$  and 17 mol percent unreacted starting materials. The HF treatment was repeated (again for 2 hours) and the nonvolatile residue (2.980 g, weight calcd for 9.82 mmol of  $\text{NF}_4\text{SnF}_5 = 2.982$  g) was shown by infrared, Raman, and  $^{19}\text{F}$  nmr spectroscopy to be essentially pure  $\text{NF}_4\text{SnF}_5$ . Anal. Calcd for  $\text{NF}_4\text{SnF}_5$ :  $\text{NF}_3$ , 23.38; Sn, 39.08. Found:  $\text{NF}_3$ , 23.6; Sn, 38.7.

When a mixture of  $\text{NF}_4\text{BF}_4$  and  $\text{SnF}_4$  in a mol ratio of 2:1 was treated 8 times, as described above, with liquid HF for a total of 35 days, the resulting nonvolatile residue consisted mainly of  $\text{NF}_4\text{SnF}_5$ , unreacted  $\text{NF}_4\text{BF}_4$ , and a small amount of  $(\text{NF}_4)_2\text{SnF}_6$ .

### Results and Discussion

Syntheses. As pointed out in the introduction,  $\text{SnF}_4$  is polymeric with Sn being hexacoordinated. Consequently, solid  $\text{SnF}_4$  does not act as a strong Lewis acid. This was experimentally confirmed by demonstrating that mixtures of  $\text{NF}_3$ ,  $\text{F}_2$ , and  $\text{SnF}_4$ , when heated to temperatures of up to  $300^\circ$  at autogenous pressures of about 150 atm, did not show any evidence for  $\text{NF}_4^+$  formation.

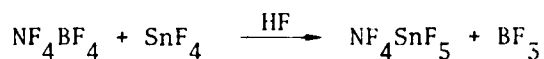
Since a direct synthesis of an  $\text{NF}_4^+$  salt derived from  $\text{SnF}_4$  was not possible, we have studied metathetical and displacement reactions. Because it has previously been shown<sup>12</sup> that  $\text{SnF}_6^{--}$  salts are stable in anhydrous HF, the metathetical and displacement reactions were carried out in this solvent. Based on the reported solubilities of  $\text{CsSbF}_6$  (5.6 g/100 g HF)<sup>6</sup>,  $\text{NF}_4\text{SbF}_6$  (280 g/100 g HF)<sup>6</sup>,  $\text{Cs}_2\text{SnF}_6$  (~250 g/100 g HF)<sup>12</sup>, and the predicted high solubility of  $(\text{NF}_4)_2\text{SnF}_6$  (the analogous  $(\text{NF}_4)_2\text{GeF}_6$  is very soluble in HF)<sup>2</sup>, the following methathetical reaction



should be capable of producing  $(\text{NF}_4)_2\text{SnF}_6$  in a purity of about 93 mol percent. The soundness of these predictions was experimentally verified. A product was obtained which based on its elemental analysis had the composition (mol %):  $(\text{NF}_4)_2\text{SnF}_6$ , 82.8;  $\text{NF}_4\text{SbF}_6$ , 12.9;  $\text{CsSbF}_6$ , 4.3. Whereas the amount of  $\text{CsSbF}_6$  found in the product approximates that predicted, the presence of about 13 percent  $\text{NF}_4\text{SbF}_6$  indicates the loss of some  $\text{Cs}_2\text{SnF}_6$ . This was probably caused by the hold up of some of the  $\text{Cs}_2\text{SnF}_6$  solution in trap I (see Figure 1) during its transfer to trap II. It should be possible to eliminate most of the  $\text{NF}_4\text{SbF}_6$  from the product by either minimizing the relative loss of  $\text{Cs}_2\text{SnF}_6$  during transfer by scaling up the reaction or by recrystallization of the product. However, both approaches were beyond the scope of the present study.

Whereas  $\text{SnF}_4$  is quite insoluble in anhydrous HF (contrary to a previous literature report<sup>13</sup>), it dissolves reasonably fast in HF solutions containing an excess of an alkali metal fluoride with formation of the corresponding alkali metal  $\text{SnF}_6^{--}$  salt.  $\text{SnF}_4$  has also been reported to act as a relatively strong acid in HF solution.<sup>13</sup> Furthermore,  $\text{GeF}_4$  is capable of displacing  $\text{BF}_4^-$  in  $\text{NF}_4\text{BF}_4$ ,<sup>2</sup> and the strength of a Lewis acid generally increases within a group of the periodic system with increasing atomic weight of the central atom. Consequently,  $\text{SnF}_4$  in HF might be expected to also be capable of displacing  $\text{BF}_4^-$  in  $\text{NF}_4\text{BF}_4$ .

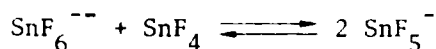
When equimolar mixtures of  $\text{NF}_4\text{BF}_4$  and  $\text{SnF}_4$  were stirred in anhydrous HF, the following quantitative reaction occurred:



However,  $\text{BF}_3$  interacts with HF and the above reaction appears to be an equilibrium reaction. Consequently, it was found advantageous to pump off the volatile products and to repeat the HF treatment at least once to obtain complete conversion to  $\text{NF}_4\text{SnF}_5$ . No evidence for  $\text{SnF}_6^{--}$  formation was observed under these conditions. The quantitative formation of  $\text{SnF}_5^-$  was surprising, since for the alkali metal fluoride -  $\text{SnF}_4$  systems exclusive  $\text{SnF}_6^{--}$  formation was observed during our study. We could not find any previous literature reports on  $\text{SnF}_5^-$ , except for a recent low-temperature  $^{19}\text{F}$  nmr study by Dean<sup>14</sup> which demonstrated the presence of polyanions in  $\text{SO}_2$  solutions of mixtures of  $\text{SnF}_6^{--}$  and  $\text{SnF}_4$ .



The possibility of preparing  $(\text{NF}_4)_2\text{SnF}_6$  from a 2:1 mixture of  $\text{NF}_4\text{BF}_4$  and  $\text{SnF}_4$  was examined. However, even after 8 HF treatments for a total of 35 days only a small amount of  $\text{SnF}_6^{--}$  had formed. The main products were  $\text{NF}_4\text{SnF}_5$  and unreacted  $\text{NF}_4\text{BF}_4$ . These results indicate that the Lewis acid strength of  $\text{SnF}_5^-$  in HF is insufficient to displace most of the  $\text{BF}_4^-$  from its  $\text{NF}_4^+$  salt and that, in agreement with Dean's observations for  $\text{SO}_2$  solutions,<sup>14</sup> the equilibrium is shifted far to the right.



Properties. Both salts,  $(\text{NF}_4)_2\text{SnF}_6$  and  $\text{NF}_4\text{SnF}_5$ , are white, stable, crystalline, moisture sensitive solids. As previously pointed out,<sup>2</sup> the onset of thermal decomposition is difficult to define for  $\text{NF}_4^+$  salts owing to the absence of a sharp decomposition point. For the  $\text{SnF}_4$  salts, one of the decomposition products is nonvolatile solid  $\text{SnF}_4$  and, therefore, no melting point could be observed. Visual observation for  $(\text{NF}_4)_2\text{SnF}_6$  in sealed glass capillaries indicated the first signs of decomposition at about 240°. The occurrence of decomposition in this temperature range was confirmed by a DSC study which showed the onset of an irreversible endotherm at about 225° which was accompanied by  $\text{F}_2$  evolution. Furthermore, sealed glass capillaries, when heated above 300°, exploded due to pressure build up from the gaseous decomposition products. For  $\text{NF}_4\text{SnF}_5$  in a sealed glass capillary, slight shrinkage of the solid was observed at about 120°. The DSC curve did not show any evidence for a sharp change in slope up to a temperature of about 270°, where a large exotherm started. It should be kept in mind, however, that for powerful oxidizers, such as  $\text{NF}_4^+$  salts, exotherms can be caused by reaction of the oxidizer with the aluminum sample container.

The hydrolyses of  $(\text{NF}_4)_2\text{SnF}_6$  and  $\text{NF}_4\text{SnF}_5$  proceeds, as previously established for other  $\text{NF}_4^+$  salts,<sup>2,15</sup> with quantitative  $\text{NF}_3$  evolution. This reaction was also used for the elemental analyses. In anhydrous HF, the  $(\text{NF}_4)_2\text{SnF}_6$  salt is highly soluble, whereas  $\text{NF}_4\text{SnF}_5$  is of moderate solubility. Both salts are also soluble in  $\text{BrF}_5$ , however the solubilities are considerably lower than those in HF.

X-Ray Powder Data. The powder pattern of  $(\text{NF}_4)_2\text{SnF}_6$  is given as supplementary material. The observed pattern, after correction for several weak lines due to the presence of the metathesis by-products  $\text{NF}_4\text{SbF}_6^1$  and  $\text{CsSbF}_6^{16}$ , is very similar to that<sup>2</sup> of  $(\text{NF}_4)_2\text{GeF}_6$ , indicating that the two compounds are isotypic. The pattern was indexed for a tetragonal unit cell, and the resulting crystallographic parameters of  $(\text{NF}_4)_2\text{SnF}_6$  are compared in Table I with those of other  $\text{NF}_4^+$  salts. As can be seen, the agreement is excellent. Since  $(\text{NF}_4)_2\text{GeF}_6$  has been prepared in high purity and is well characterized,<sup>2</sup> the x-ray powder data establish beyond doubt that the major crystalline product from the  $\text{NF}_4\text{SbF}_6 + \text{Cs}_2\text{SnF}_6$  metathesis is indeed  $(\text{NF}_4)_2\text{SnF}_6$ .

The powder pattern of  $\text{NF}_4\text{SnF}_5$  was also recorded and is given as supplementary material. It did not contain any lines which could be attributed to either  $\text{NF}_4\text{BF}_4$ ,<sup>2</sup>  $\text{SnF}_4$ , or  $(\text{NF}_4)_2\text{SnF}_6$ . Reliable indexing of the pattern was not possible owing to the large number of observed lines, but it somewhat resembles that previously observed<sup>2</sup> for  $\text{NF}_4\text{GeF}_5$ .

NMR Spectra. The  $^{19}\text{F}$  nmr spectra were recorded for both  $(\text{NF}_4)_2\text{SnF}_6$  and  $\text{NF}_4\text{SnF}_5$  in  $\text{BrF}_5$  solution. In spite of its higher melting point ( $-60.5^\circ$ ) and lower solubilities, this solvent was preferred over  $\text{HF}$ , because it was found difficult<sup>2</sup> to suppress rapid fluoride exchange between  $\text{HF}$  and the anions. In  $\text{BrF}_5$  solution, no such problems were encountered. Well resolved spectra were observed for both the  $\text{NF}_4^+$  cation and the corresponding anions, in addition to the sharp quintet ( $\delta = -272$ ) and doublet ( $\delta = -136$ ) with  $J_{\text{FF}} = 74.7$  Hz characteristic for  $\text{BrF}_5$ .<sup>2,17</sup> For both the  $(\text{NF}_4)_2\text{SnF}_6$  and the  $\text{NF}_4\text{SnF}_5$  solution a triplet of equal intensity with  $\delta = -220$ ,  $J_{\text{NF}} = 229.6$  Hz, and a line width at half height of about 5 Hz was observed which is characteristic for tetrahedral  $\text{NF}_4^+$ .<sup>2,15,18</sup> The  $(\text{NF}_4)_2\text{SnF}_6$  solution showed in addition to these resonances a narrow singlet at  $\delta = 149$  with the appropriate  $^{117/119}\text{Sn}$  satellites (average  $J_{\text{SnF}} = 1549$  Hz). These values are in good agreement with those previously reported<sup>14,19</sup> for octahedral  $\text{SnF}_6^{--}$  in different solvents. This assignment was further confirmed by recording the spectrum of  $\text{Cs}_2\text{SnF}_6$  in  $\text{BrF}_5$  solution.

Table I. Crystallographic Data of  $(\text{NF}_4)_2\text{SnF}_6$  Compared to Those of Other  $\text{NF}_4^+$  Salts

|                                 | Tetragonal Unit Cell Dimensions |                    |                      | Z    | Volume ( $\text{\AA}^3$ )<br>per F | Calcd Density<br>( $\text{g/cm}^3$ ) |
|---------------------------------|---------------------------------|--------------------|----------------------|------|------------------------------------|--------------------------------------|
|                                 | a ( $\text{\AA}$ )              | c ( $\text{\AA}$ ) | V ( $\text{\AA}^3$ ) |      |                                    |                                      |
| $\text{NF}_4\text{PF}_6^a$      | 7.577                           | 5.653              | 324.53               | 2    | 16.23                              | 2.41                                 |
| $\text{NF}_4\text{AsF}_6^a$     | 7.70                            | 5.73               | 339.73               | 2    | 16.99                              | 2.72                                 |
| $\text{NF}_4\text{SbF}_6^a$     | 7.903                           | 5.806              | 362.63               | 2    | 18.13                              | 2.98                                 |
| $\text{NF}_4\text{BiF}_6^a$     | 8.006                           | 5.821              | 373.10               | 2    | 18.66                              | 3.68                                 |
| $\text{NF}_4\text{BF}_4^b$      | 9.944                           | 5.229              | 517.04               | 4    | 16.16                              | 2.27                                 |
| $(\text{NF}_4)_2\text{GeF}_6^b$ | 10.627                          | 11.114             | 1255.14              | 16/3 | 16.81                              | 2.59                                 |
| $(\text{NF}_4)_2\text{SnF}_6$   | 10.828                          | 11.406             | 1337.35              | 16/3 | 17.91                              | 2.73                                 |

(a) Ref. 1

(b) Ref. 2

Two resonances were observed for  $\text{SnF}_5^-$  of  $\text{NF}_4\text{SnF}_5$  at  $\delta = 145.4$  and  $162.4$ , respectively, with an area ratio of 1:4. At  $-20^\circ$  the resonances consisted of broad lines, but at lower temperatures the  $\delta = 162.4$  signal showed splittings. These splittings exhibited a pronounced temperature dependence (see Figure 2). The observed spectrum can be interpreted by comparison with the data previously reported<sup>14</sup> by Dean for  $(\text{SnF}_5)_n^{n-}$  in  $\text{SO}_2$  solution. For this ion, Dean observed a singlet at  $140.4$  ppm and two approximately 1:2:1 triplets at  $154.2$  and  $158.1$  ppm, respectively, with area ratios of 1:2:2. The lower field triplet was broader than the higher field triplet and the coupling constant was  $58$  Hz. These data unambiguously showed<sup>14</sup> that  $(\text{SnF}_5)_n^{n-}$  must have a polymeric structure consisting of cis fluorine bridged  $\text{SnF}_6$  octahedrons. Our data for  $(\text{SnF}_5)_n^{n-}$  in  $\text{NF}_4\text{SnF}_5$  are quite similar with the only exception that the difference in chemical shift between the two triplets has decreased and decreases further with decreasing temperature. Thus the resonance at  $164.2$  ppm (area 4) can be interpreted as an  $\text{A}_2\text{B}_2$  system strongly distorted by second order effects.<sup>20</sup> The singlet at  $145.4$  ppm (area 1) must then be due to the bridging fluorines. The 4:1 area ratio results from the fact that only the two bridging fluorines are shared by two octahedrons. As found by Dean, the coupling between the axial and the terminal equatorial fluorines is much larger (about  $40$ - $60$  Hz) than that between the terminal and the bridging fluorines. Furthermore, the lower field half of the  $162.4$  ppm resonance shows a greater line width than the upper half, indicating weak, but differing, coupling between the bridging and the two types of terminal fluorines.

Our observations for  $\text{NF}_4\text{SnF}_5$  are in excellent agreement with the data of Dean<sup>14</sup> and demonstrate the polymeric cis fluorine bridged nature of  $\text{SnF}_5^-$ . However, we are less confident than Dean that in  $(\text{SnF}_5)_n^{n-}$ ,  $n$  equals 2. Higher values of  $n$  can certainly not be excluded and  $n$  might vary within and from sample to sample, as indicated by varying solubilities observed for different samples during this study. Attempts were unsuccessful to observe the spectrum of a 1:1 mol ratio mixture of  $\text{Cs}_2\text{SnF}_6$  and  $\text{SnF}_4$  in  $\text{BrF}_5$  solution owing to its low solubility. Only a signal due to  $\text{SnF}_6^{--}$  was observed.

Vibrational Spectra. The infrared and Raman spectra of  $(\text{NF}_4)_2\text{SnF}_6$  and  $\text{NF}_4\text{SnF}_5$  were recorded and are shown in Figures 3 and 4, respectively. The observed frequencies and their assignments are listed in Tables II and III. Comparison with the known spectra<sup>1,2</sup> of other  $\text{NF}_4^+$  salts clearly demonstrates the presence of tetrahedral  $\text{NF}_4^+$  cations, and the bands due to  $\text{NF}_4^+$  can be easily assigned. The observation of small splittings for the degenerate modes of  $\text{NF}_4^+$  and the observation of the ideally infrared inactive  $\nu_1(\text{A}_1)$  mode as a very weak band in the infrared spectra indicate that the site symmetry of  $\text{NF}_4^+$  in these solids is lower than  $\text{T}_d$ . This is not surprising in view of the above given x-ray powder data, and has previously been also observed<sup>1,2</sup> for other  $\text{NF}_4^+$  salts.

The assignments for the anion bands in  $(\text{NF}_4)_2\text{SnF}_6$  are also straightforward. The vibrational spectra of octahedral  $\text{SnF}_6^{--}$  are well known<sup>19,21-24</sup> and establish the presence of  $\text{SnF}_6^{--}$  in  $(\text{NF}_4)_2\text{SnF}_6$  (see Table II).

The anion spectrum in  $\text{NF}_4\text{SnF}_5$  shows a pattern very similar to that of the anion in  $\text{NF}_4\text{GeF}_5$ . Furthermore, the general appearance of these anion spectra closely resembles the spectrum previously reported<sup>25</sup> for solid  $\text{TaF}_5$ . The structure of the latter has been established by x-ray diffraction data<sup>26</sup> as a cis fluorine bridged tetramer. Consequently, the observed vibrational spectra indicate a value of 4 for n in these  $(\text{MF}_5)_n^{n-}$  polyanions. A thorough vibrational analysis has been carried out<sup>25</sup> for tetrameric  $\text{NbF}_5$  and  $\text{TaF}_5$  by Beattie and coworkers. Using their data, we have made tentative assignments for the stretching modes of  $\text{SnF}_5^-$  and  $\text{GeF}_5^-$  based on tetrameric anions, which are given in Table V. The assumption of a low degree of polymerization, such as a cyclic tetramer, for the anions in these  $\text{NF}_4\text{MF}_5$  salts is not unreasonable in view of their appreciable solubility in solvents, such as HF or  $\text{BrF}_5$ . However, a crystal structure determination is desirable to confirm the above conclusions.

Summary. The successful syntheses of  $\text{NF}_4\text{SnF}_5$  and  $(\text{NF}_4)_2\text{SnF}_6$  demonstrate the possibility of preparing  $\text{NF}_4^+$  salts derived from nonvolatile and unreactive polymeric Lewis acids. Such salts are important for solid propellant  $\text{NF}_3\text{-F}_2$  gas generators for chemical HF-DF lasers, because they do not require the

Table II. Vibrational Spectra of Solid  $(\text{NF}_4)_2\text{SnF}_6$  Compared to Those of  $\text{Cs}_2\text{SnF}_6$

| obsd freq ( $\text{cm}^{-1}$ ) and rel intens <sup>a</sup> |                            | assignments (point group) |  |
|--|----------------------------|---------------------------|--|
| $(\text{NF}_4)_2\text{SnF}_6$                              |                            | $\text{Cs}_2\text{SnF}_6$ | $\text{SnF}_6^{--}(\text{O}_h)$                      |
| IR   | RA                         | IR                        | RA   |
| 2310 vw  |                            |                           | $2\nu_3 (\text{A}_1 + \text{E} + \text{F}_2)$        |
| 2005 vw  |                            |                           | $\nu_1 + \nu_3 (\text{F}_2)$                         |
| 1764 vw  |                            |                           | $\nu_3 + \nu_4 (\text{A}_1 + \text{E} + \text{F}_2)$ |
| 1463 vw  |                            |                           | $\nu_1 + \nu_4 (\text{F}_2)$                         |
| 1224 mw  |                            |                           | $2\nu_4 (\text{A}_1 + \text{E} + \text{F}_2)$        |
| 1160 vs  | 1158 (1.5)                 |                           | $\nu_3 (\text{F}_2)$                                 |
| 1132 sh, vw  |                            |                           | $\nu_1 + \nu_3 (\text{F}_{1u})$                      |
| 1059 vw  |                            |                           | $\nu_2 + \nu_4 (\text{F}_1 + \text{F}_2)$            |
| 1026 vw  |                            |                           | $\nu_2 + \nu_3 (\text{F}_{1u} + \text{F}_{2u})$      |
| 854 vvw  | 881 (0.1)                  |                           | $2\nu_2 (\text{A}_1 + \text{A}_2 + \text{E})$        |
| 613 mw   | 853 (10)                   |                           | $\nu_1 (\text{A}_1)$                                 |
| 605 mw   | 613 (5.0) {<br>607 (1.5) } |                           | $\nu_4 (\text{F}_2)$                                 |
| 550 vs   | 579 (8.3)                  | 573 (10)                  | $\nu_1 (\text{A}_{1g})$                              |
|  |                            | 555 vs                    | $\nu_3 (\text{F}_{1u})$                              |
|  |                            |                           | $\nu_2 (\text{E}_g)$                                 |
|  | 470 (0+) hr                | 460 (1.2)                 |  |
|  | 449 (3.1) {<br>442 (2.9) } |                           | $\nu_2 (\text{E})$                                   |
|  | 251 (3.3)                  | 249 (4.5)                 | $\nu_5 (\text{F}_{2g})$                              |
|  | 84 (0.3)                   |                           | lattice vibration                                    |

(a) uncorrected Raman intensities



addition of a clinker forming reagent. The synthesis of  $\text{NF}_4\text{SnF}_5$  was achieved by depolymerizing  $\text{SnF}_4$  in anhydrous HF and displacing  $\text{BF}_4^-$  from  $\text{NF}_4\text{BF}_4$  as  $\text{BF}_3$  gas. For the synthesis of  $(\text{NF}_4)_2\text{SnF}_6$  a metathetical process was required. Both  $\text{NF}_4^+$  salts were characterized by material balance, elemental analysis, infrared, Raman, and  $^{19}\text{F}$  nmr spectroscopy, x-ray powder diffraction data, and DSC. Whereas  $(\text{NF}_4)_2\text{SnF}_6$  contains monomeric  $\text{SnF}_6^{--}$  anions,  $\text{NF}_4\text{SnF}_5$  contains polymeric, cis fluorine bridged, hexacoordinated anions. The vibrational spectra indicate that in solid  $\text{NF}_4\text{SnF}_5$  the anion is probably present as a cyclic tetramer.

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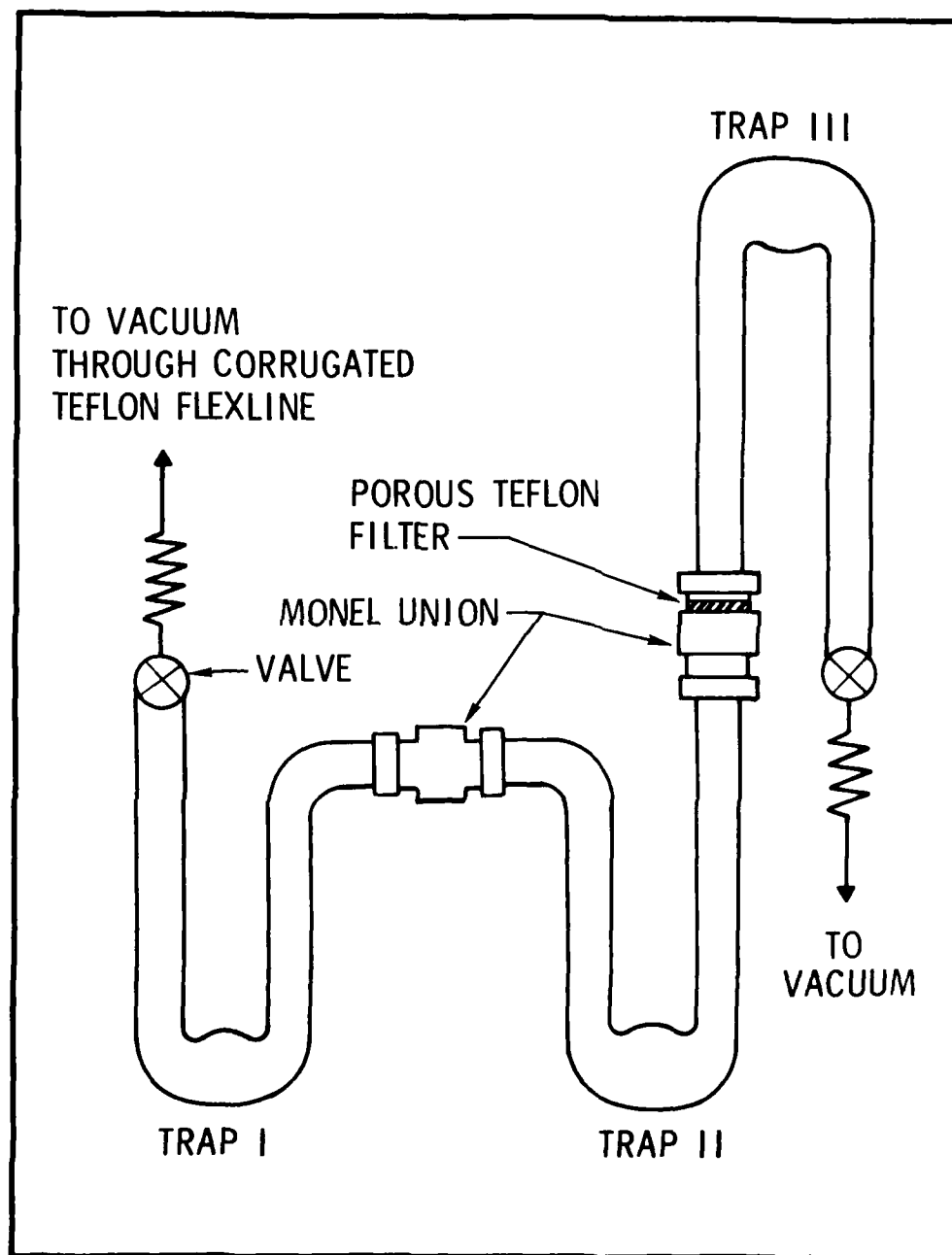
### Diagram Captions

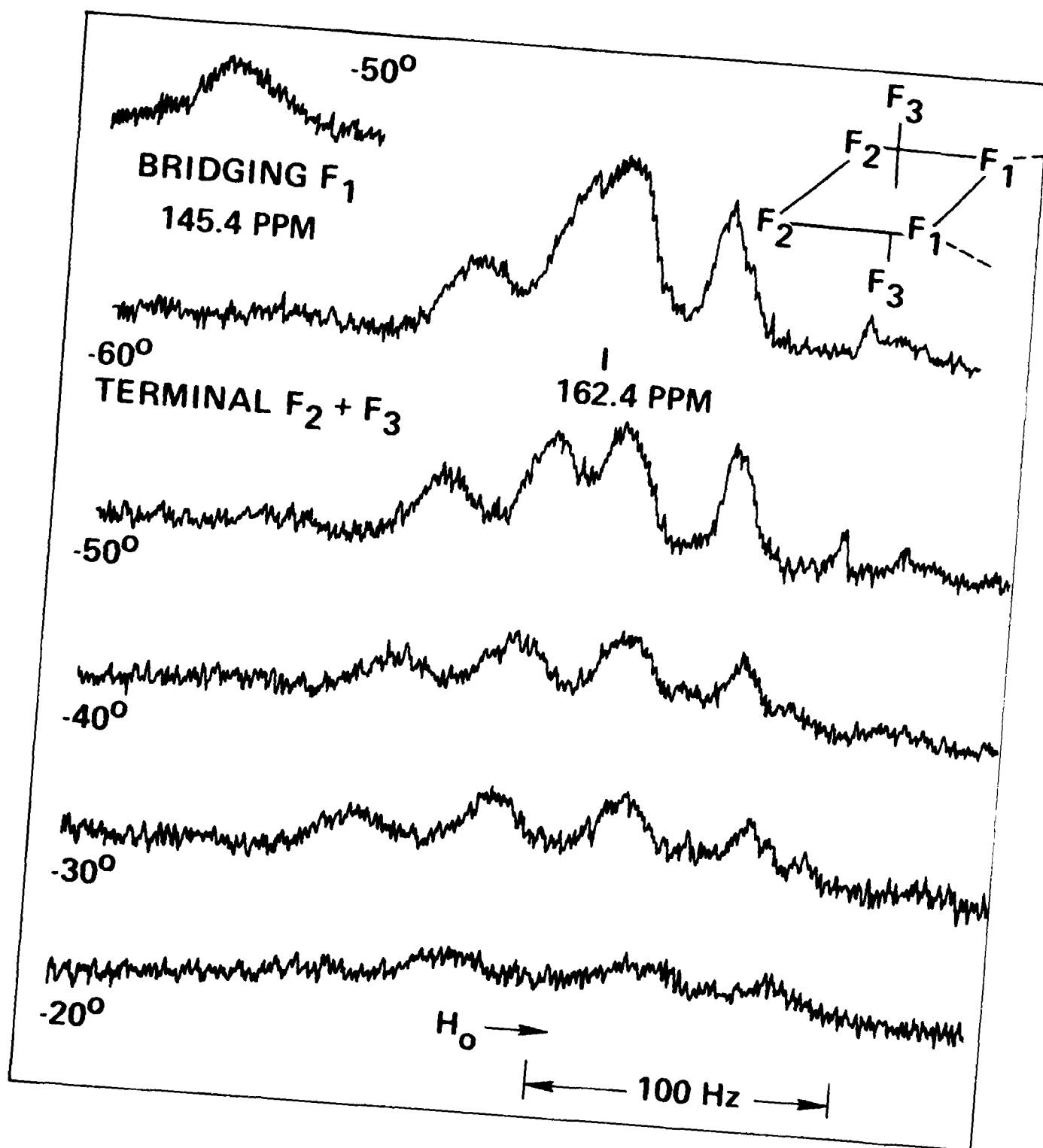
Figure 1. Apparatus for small-scale metathetical reactions consisting of three interconnected Teflon-FEP U-traps.

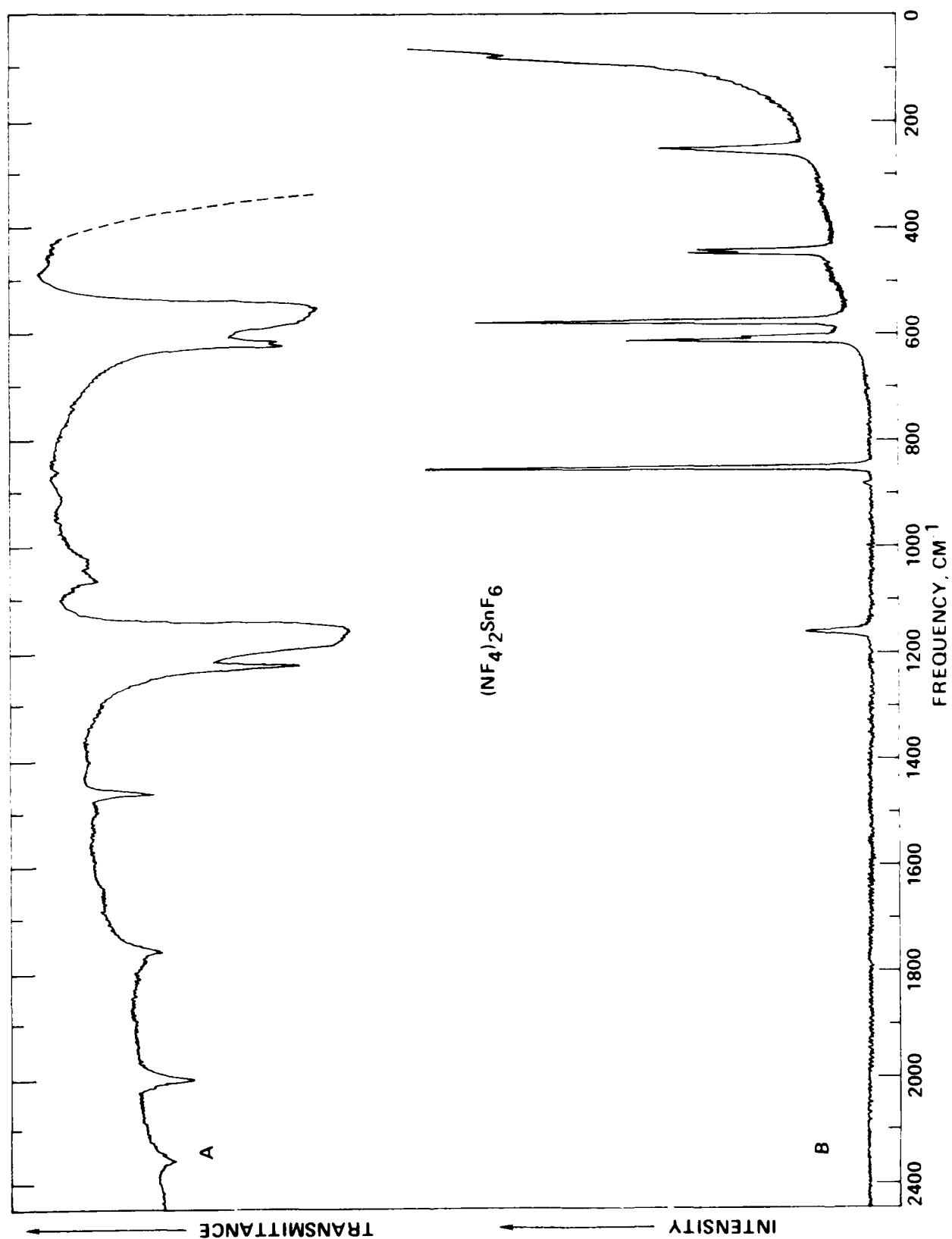
Figure 2. Temperature dependence of the  $^{19}\text{F}$  nmr spectrum of the  $(\text{SnF}_5)_n^{n-}$  part of  $\text{NF}_4\text{SnF}_5$  in  $\text{BrF}_5$  solution, recorded at 56.4 MHz using  $\text{CFCl}_3$  as external standard.

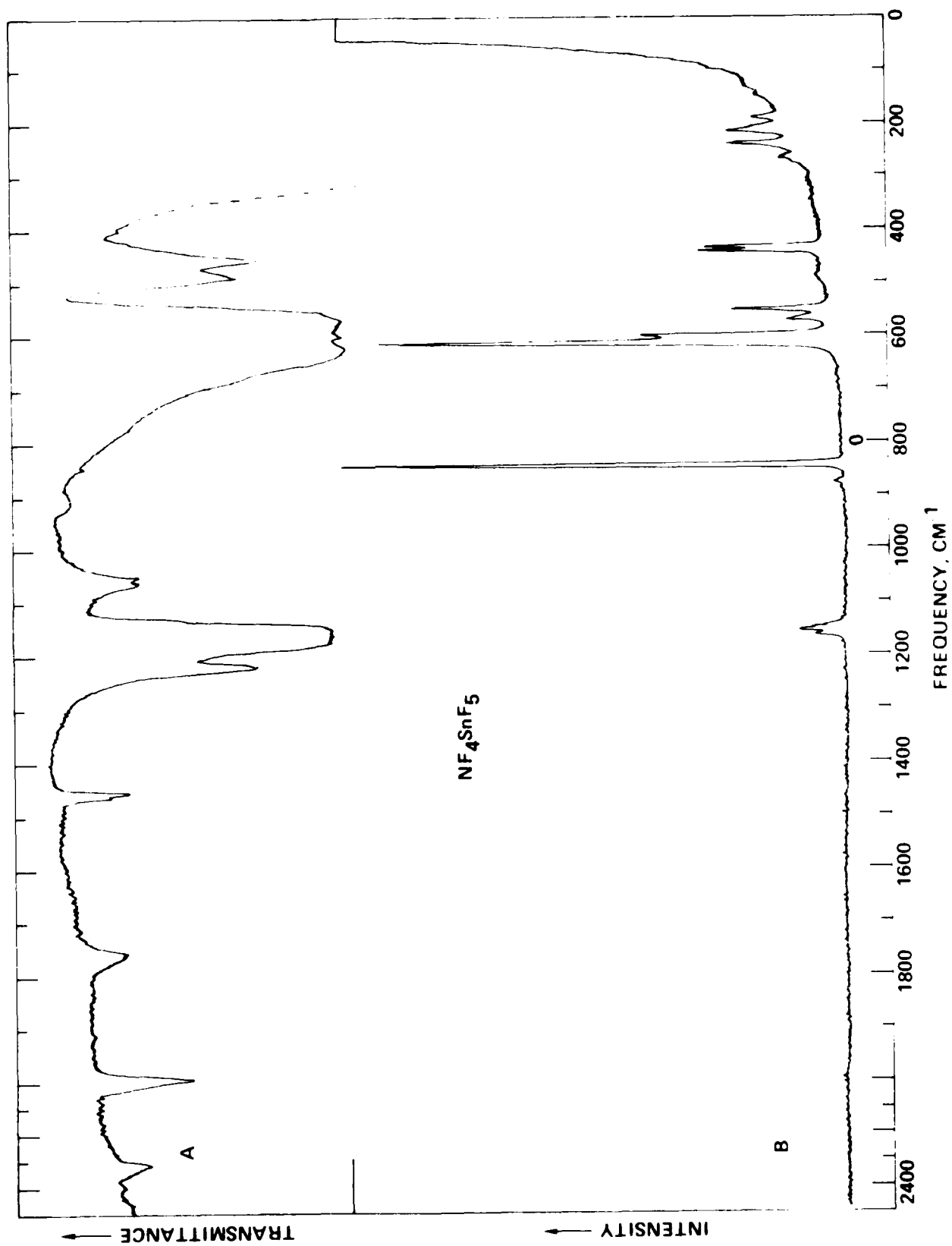
Figure 3. Vibrational spectra of solid  $(\text{NF}_4)_2\text{SnF}_6$ . Trace A: Infrared spectrum of the dry powder in a silver chloride disk; the absorption below  $400\text{ cm}^{-1}$  (broken line) is due to the  $\text{AgCl}$  windows. Trace B: Raman spectrum recorded at a spectral slit width of  $3\text{ cm}^{-1}$ . Weak bands due to  $\text{SbF}_6^-$  were deleted from the spectra.

Figure 4. Vibrational spectra of solid  $\text{NF}_4\text{SnF}_5$ , recorded under the same conditions as those of Figure 3.









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Contribution from Rocketdyne, A Division of  
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Synthesis and Characterization of  $(\text{NF}_4)_2\text{TiF}_6$  and of  
Higher  $\text{NF}_4^+$  and  $\text{Cs}^+$  Polyperfluorotitanate (IV) Salts

Karl O. Christe\* and Carl J. Schack

Received . . . . .

Abstract

Metathesis between  $\text{Cs}_2\text{TiF}_6$  and  $\text{NF}_4\text{SbF}_6$  in HF solution was used to prepare the novel perfluoroammonium salt  $(\text{NF}_4)_2\text{TiF}_6$ . The compound is a white crystalline solid, stable to about 200°. It was characterized by elemental analysis and infrared, Raman and  $^{19}\text{F}$  nmr spectroscopy. X-ray powder data show that the compound (tetragonal,  $a = 10.715\text{\AA}$ ,  $c = 11.114\text{\AA}$ ) is isotypic with  $(\text{NF}_4)_2\text{GeF}_6$  and  $(\text{NF}_4)_2\text{SnF}_6$ . Thermal or HF solution displacement reactions between  $\text{NF}_4\text{BF}_4$  and  $\text{TiF}_4$  produced the polyperfluorotitanate (IV) salts  $\text{NF}_4\text{Ti}_2\text{F}_9$  and  $\text{NF}_4\text{Ti}_3\text{F}_{13}$ . Heating of  $\text{NF}_3$ ,  $\text{F}_2$ , and  $\text{TiF}_4$  to 190° at an autogenous pressure of 160 atm produced a salt of the approximate composition  $\text{NF}_4\text{Ti}_6\text{F}_{25}$ . For comparison,  $\text{TiF}_4$  and the salts  $\text{Cs}_2\text{TiF}_6$ ,  $\text{Cs}_2\text{Ti}_2\text{F}_{10}$  and  $\text{CsTi}_2\text{F}_9$  were synthesized and characterized by vibrational spectroscopy.

Introduction

Although the nonexistence of an  $\text{NF}_5$  parent molecule and the high ionization potentials of  $\text{NF}_3$  and fluorine made the original synthesis of  $\text{NF}_4^+$  salts difficult,<sup>1</sup> their surprisingly high thermal stability permits the syntheses of salts of relatively weak Lewis acids. Thus, the preparation of stable



$\text{NF}_4^+$  salts <sup>2,3</sup> containing  $\text{GeF}_5^-$ ,  $\text{GeF}_6^{--}$ ,  $\text{SnF}_5^-$ , and  $\text{SnF}_6^{--}$  anions has been recently reported. Since  $\text{NF}_4^+$  salts are of significant interest for solid propellant  $\text{NF}_3\text{-F}_2$  gas generators <sup>4</sup> for chemical HF-DF lasers, the synthesis of novel higher performing  $\text{NF}_4^+$  salts is desirable. In this paper, we report on the syntheses and properties of  $\text{NF}_4^+$  salts derived from  $\text{TiF}_4$ .

### Experimental

Materials and Apparatus. The equipment and handling procedures used in this work were identical to those previously described. <sup>2-4</sup> The CsF was fused in a platinum crucible and powdered in the dry box. The  $\text{NF}_3$  and  $\text{F}_2$  were prepared at Rocketdyne, the HF (Matheson) was dried as previously described, <sup>5</sup> and the  $\text{BrF}_5$  (Matheson) was purified by fractional condensation prior to use. Pure  $\text{NF}_4\text{BF}_4$  was prepared from  $\text{NF}_3$ ,  $\text{F}_2$ , and  $\text{BF}_3$  by uv-photolysis <sup>2</sup> at  $-196^\circ$  and the  $\text{NF}_4\text{SbF}_6$  was synthesized as previously described. <sup>4</sup> A 10 year old sample of commercial  $\text{TiF}_4$  (Allied) had undergone partial hydrolysis, but was converted back to pure  $\text{TiF}_4$  by fluorinating it in a Monel cylinder for 2 days at  $250^\circ$  with  $\text{F}_2$  at 70 atm pressure. Both, treated and untreated, samples of  $\text{TiF}_4$  were used in the displacement reactions with  $\text{NF}_4\text{BF}_4$ . In some cases the course of the reactions was influenced by the choice of the  $\text{TiF}_4$ .

Synthesis of  $\text{Cs}_2\text{TiF}_6$ . Dry CsF (40.3 mmol) and  $\text{TiF}_4$  (20.15 mmol) were combined in a passivated Teflon FEP ampule. Anhydrous HF (3 ml liquid) was added at  $-78^\circ$ . The mixture was warmed to  $24^\circ$  and stirred for 1 hour until all solid material had dissolved. The volatile materials were pumped off at  $70^\circ$  for 2 hours. The white solid residue (8.621 g, weight calcd for 20.15 mmol of  $\text{Cs}_2\text{TiF}_6$  = 8.619 g) was shown by infrared and Raman spectroscopy to be  $\text{Cs}_2\text{TiF}_6$  of excellent purity. The products obtained from both, untreated and pre-fluorinated  $\text{TiF}_4$ , were undistinguishable. The solubility of  $\text{Cs}_2\text{TiF}_6$  in anhydrous HF at  $24^\circ$  was found to be about 4 g per g of HF.

Synthesis of  $\text{Cs}_2\text{Ti}_2\text{F}_{10}$ . This salt was synthesized from equimolar amounts of  $\text{Cs}_2\text{TiF}_6$  and prefluorinated  $\text{TiF}_4$  by either heating in a Monel cylinder to  $180^\circ$  for 7 days or by stirring the mixture in liquid anhydrous HF for 4 days at

25° and pumping off the volatile material at 50° for 3 hours. The observed weights closely corresponded to those expected for  $\text{Cs}_2\text{Ti}_2\text{F}_{10}$ . Vibrational spectroscopy showed only small amounts of  $\text{TiF}_6^{--}$  and  $\text{Ti}_2\text{F}_9^-$  for the product of the thermal reaction and of  $\text{TiF}_4$ ,  $\text{Ti}_2\text{F}_9^-$ ,  $\text{TiF}_6^{--}$ , and a higher polyanion (Ra band at  $778\text{ cm}^{-1}$ ) for the HF displacement reaction.

Synthesis of  $\text{CsTi}_2\text{F}_9$ . This salt was prepared as described above for  $\text{Cs}_2\text{Ti}_2\text{F}_{10}$ , except for using  $\text{Cs}_2\text{TiF}_6$  and  $\text{TiF}_4$  in a 1:3 mole ratio. Vibrational spectroscopy showed that the product from the HF reaction contained mainly  $\text{Ti}_2\text{F}_9^-$  with traces of  $\text{TiF}_4$  and  $\text{Ti}_2\text{F}_{10}^{--}$  being present. The product from the thermal reaction was a mixture of approximately  $4\text{TiF}_4$ ,  $4\text{CsTi}_2\text{F}_9$ , and  $2\text{Cs}_2\text{Ti}_2\text{F}_{10}$ .

The synthesis of higher polyperfluorotitanate (IV) anions was attempted by heating a 1:5 mol ratio mixture of  $\text{Cs}_2\text{TiF}_6$  and  $\text{TiF}_4$  to 180° for 7 days. Vibrational spectroscopy, however, showed the presence of only  $\text{Ti}_2\text{F}_{10}^{--}$ ,  $\text{Ti}_2\text{F}_9^-$ , and unreacted  $\text{TiF}_4$ .

Synthesis of  $(\text{NF}_4)_2\text{TiF}_6$ . The metathetical synthesis of  $(\text{NF}_4)_2\text{TiF}_6$  from saturated HF solutions of  $\text{NF}_4\text{SbF}_6$  (10.00 mmol) and  $\text{Cs}_2\text{TiF}_6$  (5.00 mmol) was carried out in the apparatus previously described<sup>3</sup> for the synthesis of  $(\text{NF}_4)_2\text{SnF}_6$ . After combination of the solutions of the two starting materials at room temperature and formation of a  $\text{CsSbF}_6$  precipitate, the mixture was cooled to -78° and filtered. The volatile materials were pumped off at 50° for 1 hour. The filter cake (3.85 g) was shown by its x-ray powder diffraction pattern and vibrational spectroscopy to be mainly  $\text{CsSbF}_6$  containing, due to the hold up of some mother liquor, a small amount of  $(\text{NF}_4)_2\text{TiF}_6$ . The filtrate residue (1.55 g, weight calcd for 5 mmol of  $(\text{NF}_4)_2\text{TiF}_6 = 1.71\text{ g}$ ) had the composition (mol %): 88.5  $(\text{NF}_4)_2\text{TiF}_6$  and 11.5  $\text{CsSbF}_6$ . Found:  $\text{NF}_3$ , 8.77; Ti, 12.21; Sb, 4.11; Cs, 4.4. Calcd for a mixture of 88.5  $(\text{NF}_4)_2\text{TiF}_6$  and 11.5  $\text{CsSbF}_6$ :  $\text{NF}_3$ , 8.72; Ti, 12.29; Sb, 4.06; Cs, 4.43. Based on the observed Raman spectrum, the composition of the filtrate residue was estimated to be 90  $(\text{NF}_4)_2\text{TiF}_6$  and 10  $\text{CsSbF}_6$ , in good agreement with the above elemental analysis.

Displacement Reactions between  $\text{NF}_4\text{BF}_4$  and  $\text{TiF}_4$ . These displacement reactions were carried out either in HF solution at room temperature or by heating the starting materials in the absence of a solvent in a Monel cylinder: For the HF solution reactions, the solid starting materials (6 mmol of  $\text{NF}_4\text{BF}_4$  in each experiment) were placed in a passivated Teflon FEP ampoule and 15 ml of liquid anhydrous HF was added. The mixture was stirred with a Teflon coated magnetic stirring bar at room temperature for a given time period. The volatile products were pumped off at 50° for 3 hours and the composition of the solid residue was determined by elemental and spectroscopic analyses and from the observed material balances.

The thermal displacement reactions were carried out in a prepassivated 90 ml Monel cylinder which was heated in an electric oven for a specified time period. The volatile products were separated by fractional condensation in a vacuum line, measured by PVT, and identified by infrared spectroscopy. The solid residues were weighed and characterized by elemental and spectroscopic analyses. The results of these experiments are summarized in Table 1.

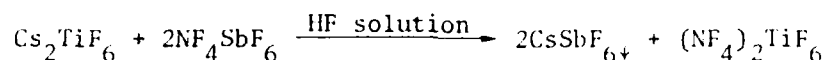
Direct Synthesis of  $\text{NF}_4^+$  Polyperfluorotitanates (IV). Prefluorinated  $\text{TiF}_4$  (11.3 mmol),  $\text{NF}_3$  (200 mmol), and  $\text{F}_2$  (200 mmol) were heated in a passivated 90 ml Monel cylinder to various temperatures for different time periods. After each heating cycle, the volatile products were temporarily removed and the progress of the reaction was followed by determining the weight gain of the solid and recording its vibrational spectra. Heating to 200° for 3 days resulted in a weight gain of 8 mg and the vibrational spectra showed mainly unreacted  $\text{TiF}_4$  in addition to a small amount of  $\text{NF}_4^+$  and a polyperfluorotitanate (IV) anion (probably  $\text{Ti}_6\text{F}_{25}^-$ , see below) having its strongest Raman line at  $784\text{ cm}^{-1}$ . During the next two heating cycles (190-195° for 14 days and 180° for 35 days) the solid gained 149 and 41 mg, respectively, in weight. The vibrational spectra did not show any evidence of unreacted  $\text{TiF}_4$ , and the relative intensities of the bands due to  $\text{NF}_4^+$  had significantly increased. Furthermore, the  $784\text{ cm}^{-1}$  Raman line had become by far the most intense Raman line. Additional heating to 230° for 3 days did not result in significant changes in either the weight or the vibrational spectra of the solid. Based on the observed weight increase and on the lack of spectro-

scopic evidence for the presence of lower polyperfluorotitanate (IV) anions, the solid product appears to have the approximate composition  $\text{NF}_4\text{Ti}_6\text{F}_{25}$  (calcd weight increase, 205 mg; obsd weight increase 198 mg).

### Results and Discussion

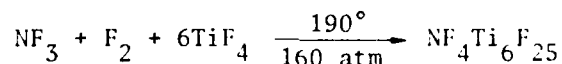
Syntheses of  $\text{NF}_4^+$  Salts. Perfluoroammonium salts of  $\text{TiF}_4$  were prepared by the following methods.

(1) Metathesis:



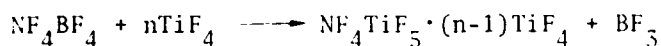
The yield of  $(\text{NF}_4)_2\text{TiF}_6$  in this reaction is practically quantitative, except for material losses caused by the retention of a certain amount of mother liquor by the filter cake. The purity of the material obtained in this manner was approximately 88.5 mol percent, the remainder being  $\text{CsSbF}_6$ .

(2) Direct synthesis from  $\text{NF}_3$ ,  $\text{F}_2$ , and  $\text{TiF}_4$ :

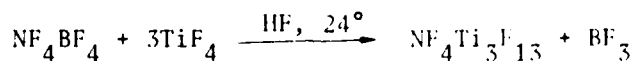


Heating of  $\text{TiF}_4$  with a large excess of  $\text{NF}_3$  and  $\text{F}_2$  to 180-195° for 50 days under an autogenous pressure of about 160 atm produced a solid of the approximate composition  $\text{NF}_4\text{Ti}_6\text{F}_{25}$ . Significant increases or decreases of the reaction temperature resulted in lower conversions of  $\text{NF}_3$  to  $\text{NF}_4^+$ .

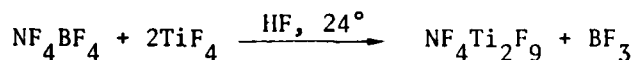
(3) Displacement reactions:



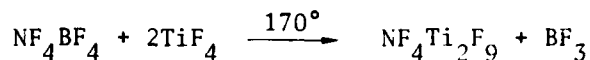
These reactions were carried out either in anhydrous HF solution at room temperature or by heating the solid starting materials in a Monel cylinder to 160-190°. The composition of the products was influenced by both the reaction conditions and the choice of the  $\text{TiF}_4$  starting material (see Table 1). For the HF solution displacement reactions, the use of pre-fluorinated  $\text{TiF}_4$  (see below) resulted in the following approximate stoichiometry, independent of the mol ratio of the starting materials:



When untreated  $\text{TiF}_4$  was used, the reaction stoichiometry changed from 1:3 to 1:2, again independent of the mol ratio of the starting materials:



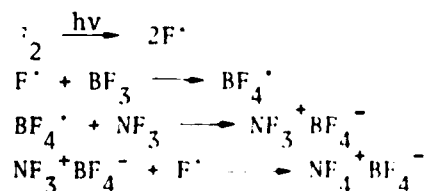
In the thermal displacement reactions, the use of prefluorinated  $\text{TiF}_4$  at  $170^\circ$  resulted in a clean 1:2 reaction between  $\text{NF}_4\text{BF}_4$  and  $\text{TiF}_4$  according to:



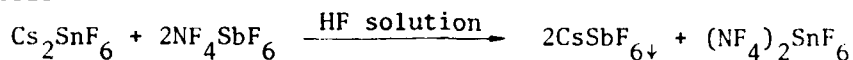
When an excess of  $\text{NF}_4\text{BF}_4$  was used, the reaction was complete in 20 hours, producing a mixture of  $\text{NF}_4\text{Ti}_2\text{F}_9$  and unreacted  $\text{NF}_4\text{BF}_4$ . Using a 1:2 mol ratio of  $\text{NF}_4\text{BF}_4$  and  $\text{TiF}_4$ , however, longer heating periods were required to avoid the formation of some  $\text{NF}_4\text{Ti}_3\text{F}_{13}$  as a by-product.

With untreated  $\text{TiF}_4$ , some of the  $\text{NF}_4^+$  salt was used up for the fluorination of the partially hydrolyzed  $\text{TiF}_4$ , however, the main product formed at  $190^\circ$  was again  $\text{NF}_4\text{Ti}_2\text{F}_9$ . When the reaction temperature was lowered to  $160^\circ$ , the main product was  $\text{NF}_4\text{Ti}_3\text{F}_{13}$ .

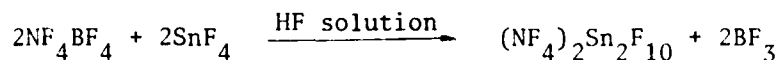
The above results are not surprising in view of our present understanding of  $\text{NF}_4^+$  chemistry. It appears that the nature of the Lewis acid determines the possible synthetic routes towards their  $\text{NF}_4^+$  salts. If a sufficiently strong Lewis acid is monomeric at the reaction temperature, a direct synthesis from  $\text{NF}_3$ ,  $\text{F}_2$ , and the Lewis acid is possible. The initial step in this direct synthesis is the generation of F atoms <sup>1</sup> from  $\text{F}_2$  by either discharge,<sup>6,7</sup> radiation,<sup>1,1,8</sup> or heating.<sup>4,9</sup> These F atoms then react with the monomeric Lewis acid to form a Lewis acid·F radical,<sup>10</sup> a species which might be capable <sup>1,11</sup> of supplying the energy (ionization potential of  $\text{NF}_3$  minus the energy released by the formation of the ion pair) required for the oxidation of  $\text{NF}_3$  to  $\text{NF}_3^+$ . The latter cation can then be readily fluorinated by either F· or  $\text{F}_2$  to  $\text{NF}_4^+$ . A typical example for this scheme is the low temperature uv photolysis of the  $\text{NF}_3\text{-F}_2\text{-BF}_3$  system: <sup>1,1,11</sup>



On the other hand, if the Lewis acid is polymeric at temperatures above the thermal decomposition point of its  $\text{NF}_4^+$  salt, indirect synthetic methods must be used. A typical example is  $\text{SnF}_4$  (sublimation point  $704^\circ$ ), where metathesis



and the displacement reaction



have successfully been applied <sup>3</sup> to the syntheses of its  $\text{NF}_4^+$  salts.

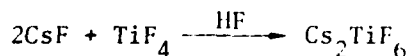
The physical properties of  $\text{TiF}_4$  (polymeric solid at room temperature with a vapor pressure of 1 atm at  $284^\circ$ ) are intermediate between those of  $\text{BF}_3$  (b.p.  $-101^\circ$ ) or  $\text{GeF}_4$  (1 atm vapor pressure at  $-36^\circ$ ) and  $\text{SnF}_4$  (b.p.  $705^\circ$ ). Consequently, the successful, although slow, direct thermal synthesis of an  $\text{NF}_4^+$  salt of  $\text{TiF}_4$  and the pronounced tendency of  $\text{TiF}_4$  to form polyanions are not unexpected. However, the actual composition of the polyanions was surprising. Whereas both  $\text{GeF}_4$  and  $\text{SnF}_4$  in their displacement reactions <sup>2,3</sup> with  $\text{NF}_4\text{BF}_4$  form exclusively the  $\text{Ge}_2\text{F}_{10}^{--}$  and  $\text{Sn}_2\text{F}_{10}^{--}$  anions, respectively, no evidence was obtained for the formation of  $\text{Ti}_2\text{F}_{10}^{--}$  in the corresponding reactions of  $\text{TiF}_4$ . Instead, only the polymeric anions  $\text{Ti}_2\text{F}_9^-$  and  $\text{Ti}_3\text{F}_{15}^-$  were observed. Since  $\text{TiF}_6^{--}$  is known <sup>1,2</sup> to associate with  $\text{TiF}_5^-$  or  $\text{TiF}_4$  to form  $\text{Ti}_2\text{F}_{11}^{3-}$  and  $\text{Ti}_2\text{F}_{10}^{--}$ , respectively, the failure to observe the two latter anions in the  $\text{NF}_4\text{BF}_4$ - $\text{TiF}_4$  displacement reactions suggests that  $\text{TiF}_6^{--}$  is not formed as an intermediate in appreciable quantities. Furthermore, the absence of observable amounts of  $\text{Ti}_2\text{F}_{10}^{--}$  indicates either that  $\text{TiF}_5^-$  preferentially associates with  $\text{TiF}_4$  rather than with itself, or that the smallest  $\text{TiF}_4$  units present which will accept a fluoride ion, are dimers. Unfortunately, the structures of both solid  $\text{TiF}_4$  and of the species present in its HF solutions are unknown. Consequently, it is at present inappropriate to rationalize the different behavior of  $\text{TiF}_4$  and of the two main group tetrafluorides.

The fact that the displacement reaction in HF solution resulted for untreated  $\text{TiF}_4$  in a lower polyanion ( $\text{Ti}_2\text{F}_9^-$ ) than for prefluorinated  $\text{TiF}_4$ , is consistent with previous reports<sup>13</sup> on the solubility of  $\text{TiF}_4$  in HF. Thus  $\text{TiF}_4$  is only sparingly soluble in anhydrous HF, but its solubility is significantly increased by the addition of a Lewis base, such as an alkali metal fluoride or water. Apparently, the base, i.e.  $\text{F}^-$  ions, helps to depolymerize the  $\text{TiF}_4$ . Since the untreated  $\text{TiF}_4$  was partially hydrolyzed, it probably generated upon addition to the HF solution some  $\text{H}_2\text{O}$ , which in the presence of HF and  $\text{TiF}_4$  would be protonated to yield  $\text{OH}_3^+$  and a polytitanate anion. No chemical interaction between  $\text{OH}_3^+$  and  $\text{NF}_4^+$  is expected, since it has previously been demonstrated that  $\text{OH}_3^+\text{SbF}_6^-$  and  $\text{NF}_4^+\text{SbF}_6^-$  can coexist in HF solution.<sup>14</sup>

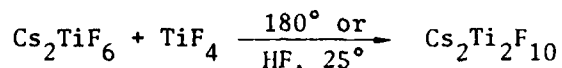
A previous study<sup>13</sup> on the relative strength of fluoroacids in HF solution had placed  $\text{BF}_3$ ,  $\text{SnF}_4$ , and  $\text{TiF}_4$  in categories 2, 3, and 5, respectively, where the acid strength decreased with increasing category number. The results from our studies, i.e. the fact that both  $\text{SnF}_4$  and  $\text{TiF}_4$  are capable of quantitatively displacing  $\text{BF}_4^-$  from  $\text{NF}_4\text{BF}_4$  in HF solution, indicate that this acid classification is not generally valid.

Syntheses of Cs Salts. For the characterization of the polyperfluorotitanate (IV) anions in their  $\text{NF}_4^+$  salts, a better knowledge of these anions was required. Very little information on polyperfluorotitanates (IV) has previously been published. Except for a recent DSC study on  $\text{NOTiF}_5$ , which was shown to decompose at  $225^\circ$  to  $\text{NOTi}_2\text{F}_9$  and  $\text{FNO}$ ,<sup>15</sup> the only detailed study on polyperfluorotitanates was carried out by Dean.<sup>12</sup> Studying the  $\text{TiF}_4 - (\text{Pr}_2\text{NH}_2)_2\text{TiF}_6$  system in  $\text{SO}_2$  solution by  $^{19}\text{F}$  nmr spectroscopy, he established the presence of the  $\text{Ti}_2\text{F}_{11}^{3-}$ ,  $\text{Ti}_2\text{F}_{10}^{--}$ , and  $\text{Ti}_2\text{F}_9^-$  anions, in addition to other unidentified polymeric anions.

Our study in anhydrous HF as a solvent showed that pure  $\text{Cs}_2\text{TiF}_6$  is formed from stoichiometric amounts of CsF and either untreated or prefluorinated  $\text{TiF}_4$ :

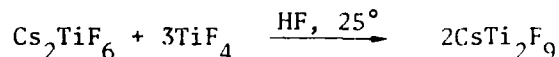


The compound  $\text{Cs}_2\text{Ti}_2\text{F}_{10}$  can be produced from an equimolar mixture of  $\text{Cs}_2\text{TiF}_6$  and  $\text{TiF}_4$  by either HF treatment at room temperature or heating of the solids to  $180^\circ$ :



Vibrational spectroscopy showed only traces of  $\text{TiF}_4$ ,  $\text{TiF}_6^{--}$ , and  $\text{Ti}_2\text{F}_9^-$ , indicating that under these conditions  $\text{Ti}_2\text{F}_{10}^{--}$  is clearly the favored species.

When the mol ratio of  $\text{Cs}_2\text{TiF}_6$  to  $\text{TiF}_4$  was changed to 1:3, the reaction in HF solution produced almost exclusively  $\text{Ti}_2\text{F}_9^-$  according to:



Only traces of  $\text{TiF}_4$  and  $\text{Ti}_2\text{F}_{10}^{--}$  were present. The thermal reaction, however, produced a mixture of approximately  $4\text{TiF}_4$ ,  $4\text{CsTi}_2\text{F}_9$ , and  $2\text{Cs}_2\text{Ti}_2\text{F}_{10}$ .

A further increase of the  $\text{TiF}_4$  ratio in the thermal reactions did not produce any evidence for the formation of polyanions higher than  $\text{Ti}_2\text{F}_9^-$ , but resulted in unreacted  $\text{TiF}_4$ . The HF solution study was not extended beyond the 1:3  $\text{Cs}_2\text{TiF}_6:\text{TiF}_4$  mol ratio.

Properties. The most interesting one of the novel salts prepared during this study is  $(\text{NF}_4)_2\text{TiF}_6$ , since it has the highest usable fluorine content of any presently known  $\text{NF}_4^+$  salt. All the  $\text{NF}_4^+$  perfluorotitanates (IV) are white crystalline solids. Based on observations of their thermal decompositions in sealed glass capillaries and on the results of the direct thermal synthesis and of the thermal displacement reactions, these  $\text{NF}_4^+$  salts are stable to at least  $200^\circ$ . By analogy with the other known  $\text{NF}_4^+$  salts, it is difficult to obtain meaningful decomposition temperatures from either m.p. determinations or DSC data.<sup>2,3</sup> All salts are hygroscopic and hydrolyze in water with quantitative  $\text{NF}_3$  and less than quantitative  $\text{O}_2$  evolution, in agreement with previous findings.<sup>2</sup> The hydrolysate shows the yellow color characteristic for titanyl salts. The  $(\text{NF}_4)_2\text{TiF}_6$  salt is highly soluble in HF and moderately soluble in  $\text{BrF}_5$ . For the polyanion salts, the solubility decreases with increasing anion size.



The  $\text{Cs}^+$  salts are also stable, white, crystalline solids. The  $\text{Cs}_2\text{TiF}_6$  salt is very soluble in HF (about 4 g/g of HF), but the solubility sharply decreases for the polyanion salts. The hydrolysis of the cesium perfluoropolytitanates (IV) was followed by Raman spectroscopy. The spectra obtained for the solid phase in equilibrium with the aqueous phase showed that the bands due to  $\text{TiF}_4$  and the higher polyanion impurities disappeared first, accompanied by a simultaneous growth of the  $\text{TiF}_6^{--}$  bands. The aqueous phase showed  $\text{TiF}_6^{--}$  as the main constituent.

X-Ray Powder Data. The powder pattern of  $(\text{NF}_4)_2\text{TiF}_6$  is listed in Table 2. After correction for weak lines due to  $\text{CsSbF}_6$  and  $\text{NF}_4\text{SbF}_6$ , all observed lines could be indexed for a tetragonal unit cell. The resulting crystallographic parameters are compared in Table 3 to those of similar  $\text{NF}_4^+$  salts. The similarity of the patterns of  $(\text{NF}_4)_2\text{TiF}_6$ ,  $(\text{NF}_4)_2\text{SnF}_6$ ,<sup>3</sup> and  $(\text{NF}_4)_2\text{GeF}_6$ <sup>2</sup> indicates that the three compounds are isotypic.

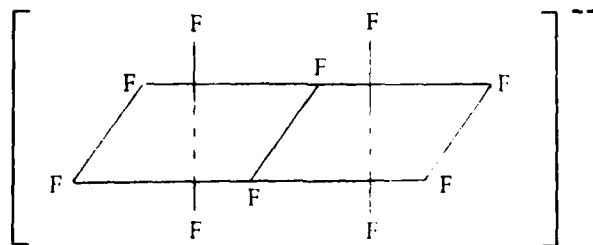
NMR Spectra. Since in HF solution rapid exchange between the solvent and the anion prevents observation of well resolved anion spectra, the  $^{19}\text{F}$  nmr spectrum of  $(\text{NF}_4)_2\text{TiF}_6$  was recorded in  $\text{BrF}_5$  solution. In addition to the solvent lines,<sup>2</sup> the spectrum showed the characteristic<sup>9,16</sup> triplet ( $\delta = -220.8$ ,  $J_{\text{NF}} = 229$  Hz) for  $\text{NF}_4^+$  and the characteristic<sup>12,17</sup>  $\text{TiF}_6^{--}$  signal at  $\delta = -81.7$ . The solubility of the  $\text{NF}_4^+$  polytitanate salts in  $\text{BrF}_5$  was too low to permit the observation of useful spectra. Since the  $^{19}\text{F}$  nmr spectra of  $\text{Ti}_2\text{F}_{11}^{3-}$ ,  $\text{Ti}_2\text{F}_{10}^{--}$ , and  $\text{Ti}_2\text{F}_9^-$  in  $\text{SO}_2$  solution have previously been studied and assigned in detail by Dean,<sup>12</sup> no further work in this direction was undertaken.

Vibrational Spectra. The infrared and Raman spectrum of solid  $(\text{NF}_4)_2\text{TiF}_6$  is shown in Figure 1. The observed frequencies are listed in Table 4. Comparison with the previously reported<sup>2-4,8,16,18</sup> spectra of other  $\text{NF}_4^+$  salts demonstrates beyond doubt the presence of the  $\text{NF}_4^+$  cation. The remaining bands are due to the anion and are in excellent agreement with those previously reported for  $\text{TiF}_6^{--}$  in  $\text{Cs}_2\text{TiF}_6$ <sup>17,19</sup> and  $(\text{HgI})_2\text{TiF}_6$ .<sup>20</sup> The observation of small splittings for some of the degenerate modes of  $\text{NF}_4^+$  indicate that the site symmetry of  $\text{NF}_4^+$  in the solid is lower than  $T_d$ . The same effect has previously been observed<sup>3</sup> for isotypic  $(\text{NF}_4)_2\text{SnF}_6$ .

The vibrational spectra of  $\text{NF}_4\text{Ti}_2\text{F}_9$ ,  $\text{NF}_4\text{Ti}_3\text{F}_{13}$ , and  $\text{NF}_4\text{Ti}_6\text{F}_{25}$  are shown in Figures 1 and 2, respectively, and the observed frequencies are listed in Table 5. Again, the presence of  $\text{NF}_4^+$  is clearly established.

For a better characterization of the anion bands, the vibrational spectra of several cesium salts and of solid  $\text{TiF}_4$  were also recorded (see Figures 3 and 4, and Tables 4-6). Since  $\text{Cs}_2\text{TiF}_6$  can be prepared in high purity and since higher polytitanate impurities preferentially underwent hydrolysis, no problems were encountered with defining the principal bands belonging to each anion. The single most useful band for the identification of a polyperfluorotitanate (IV) anion is the symmetric, in phase, terminal  $\text{TiF}$  stretching mode. This mode results in a narrow and very intense Raman band, the frequencies of which have been denoted in Figures 1-3. As can be seen, the frequency of this band increases with increasing  $\text{TiF}_4$  content and decreasing negative charge of the anion, i.e.  $\text{TiF}_6^{--} < \text{Ti}_2\text{F}_{10}^{--} < \text{Ti}_2\text{F}_9^- < \text{Ti}_3\text{F}_{13}^- < \text{Ti}_6\text{F}_{25}^- < (\text{TiF}_4)_n^-$ .

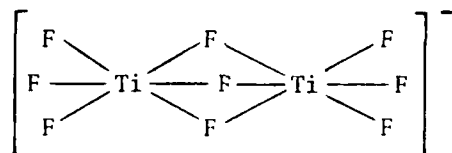
The structure of  $\text{Ti}_2\text{F}_{10}^{--}$  has been well established <sup>12</sup> by  $^{19}\text{F}$  nmr spectroscopy as the cis-fluorine bridged dimer and a thorough vibrational analysis has pre-



viously been carried <sup>21,22</sup> out for the isostructural molecule  $\text{Nb}_2\text{Cl}_{10}$ . Consequently, sufficient information was available to allow some tentative assignments for  $\text{Ti}_2\text{F}_{10}^{--}$ . These assignments are summarized in Table 6 and are based on the symmetry coordinates defined for  $\text{Nb}_2\text{Cl}_{10}$  by Beattie and coworkers.<sup>21</sup>

No attempts were made to assign the spectra of the remaining polyperfluorotitanate (IV) anions and  $\text{TiF}_4$  itself, although some data are available for  $\text{Ti}_2\text{F}_9^-$ . Dean suggested <sup>12</sup> on the basis of  $^{19}\text{F}$  nmr data for  $\text{Ti}_2\text{F}_9^-$  the triply

fluorine bridged structure and Beattie has analyzed <sup>21</sup> the vibrational spectrum



of the isostructural  $\text{Ti}_2\text{Cl}_9^{3-}$  anion. Our spectra of prefluorinated  $\text{TiF}_4$  (see Figures 3 and 4) significantly differ from those of untreated  $\text{TiF}_4$  and those <sup>23-25</sup> previously reported in the literature.

Summary. The synthesis of  $\text{NF}_4^+$  salts has successfully been extended to a subgroup element. The results of this study show that  $\text{TiF}_4$  can act as a much stronger Lewis acid than predicted on the basis of previous literature data.<sup>13</sup> Thus, stable  $\text{NF}_4^+$  salts derived from  $\text{TiF}_4$  can be prepared either directly or indirectly. Of all the presently known  $\text{NF}_4^+$  salts,  $(\text{NF}_4)_2\text{TiF}_6$  contains the highest percentage of usable fluorine and, therefore, is an excellent candidate for a solid propellant  $\text{NF}_3\text{-F}_2$  gas generator.

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### Diagram Captions

Figure 1. Vibrational spectra of solid  $(\text{NF}_4)_2\text{TiF}_6$  and  $\text{NF}_4\text{Ti}_2\text{F}_9$ . Traces A and B, infrared and Raman spectra of  $(\text{NF}_4)_2\text{TiF}_6$ , respectively. Traces C and D, corresponding spectra of  $\text{NF}_4\text{Ti}_2\text{F}_9$ , prepared by the thermal ( $170^\circ$ ) displacement reaction between  $\text{NF}_4\text{BF}_4$  and  $\text{TiF}_4$  (1:2). The absorptions below  $400\text{ cm}^{-1}$  in the infrared spectra (broken lines) are due to the AgCl windows. Weak bands, due to impurities, were deleted from the spectra. Raman spectra were recorded with a spectral slit width of  $3\text{ cm}^{-1}$ . The insert was recorded at a higher recorder gain.

Figure 2. Vibrational spectra of solid  $\text{NF}_4\text{Ti}_3\text{F}_{13}$  and  $\text{NF}_4\text{Ti}_6\text{F}_{25}$ , recorded under the same conditions as those of Figure 1. The samples of  $\text{NF}_4\text{Ti}_3\text{F}_{13}$  and  $\text{NF}_4\text{Ti}_6\text{F}_{25}$  were prepared by the displacement reaction between  $\text{NF}_4\text{BF}_4$  and prefluorinated  $\text{TiF}_4$  in HF and by direct synthesis from  $\text{NF}_3$ ,  $\text{F}_2$ , and  $\text{TiF}_4$  at  $190^\circ$ , respectively.

Figure 3. Raman spectra of solid  $\text{Cs}_2\text{TiF}_6$ ,  $\text{Cs}_2\text{Ti}_2\text{F}_{10}$ ,  $\text{CsTi}_2\text{F}_9$ , and prefluorinated  $\text{TiF}_4$ .

Figure 4. Infrared spectra of solid  $\text{Cs}_2\text{TiF}_6$ ,  $\text{Cs}_2\text{Ti}_2\text{F}_{10}$ ,  $\text{CsTi}_2\text{F}_9$ , and prefluorinated  $\text{TiF}_4$  as dry powders in AgCl disks.

Table 1. Results from the Displacement Reactions between  $\text{NF}_4\text{BF}_4$  and  $\text{TiF}_4$

| Reactants (mol)   | Reaction Conditions | Products (mol)  |
|---|---------------------|---|
| $\text{NF}_4\text{BF}_4$ (6), untreated $\text{TiF}_4$ (6)  | HF, 24°, 18h        | $\text{NF}_4\text{Ti}_2\text{F}_9$ (4), $\text{NF}_4\text{BF}_4$ (4)  |
| $\text{NF}_4\text{BF}_4$ (6), untreated $\text{TiF}_4$ (12) | HF, 24°, 72h        | $\text{NF}_4\text{Ti}_2\text{F}_9$ (6)  |
| $\text{NF}_4\text{BF}_4$ (6), prefluor. $\text{TiF}_4$ (6)  | HF, 24°, 138h       | $\text{NF}_4\text{Ti}_3\text{F}_{13}$ (~2), $\text{NF}_4\text{BF}_4$ (~4),<br>small amount of $\text{NF}_4\text{Ti}_2\text{F}_9$  |
| $\text{NF}_4\text{BF}_4$ (6), prefluor. $\text{TiF}_4$ (12) | HF, 24°, 96h        | $\text{NF}_4\text{Ti}_3\text{F}_{13}$ (4), $\text{NF}_4\text{BF}_4$ (2),  |
| $\text{NF}_4\text{BF}_4$ (6), untreated $\text{TiF}_4$ (6)  | 190°, 18h           | $\text{NF}_4\text{Ti}_2\text{F}_9$ (~3), $\text{NF}_3$ (~3), $\text{BF}_3$ (~6),<br>small amounts of $\text{NF}_4\text{BF}_4$ and $\text{NF}_4\text{Ti}_3\text{F}_{13}$ |
| $\text{NF}_4\text{BF}_4$ (6), untreated $\text{TiF}_4$ (6)  | 160°, 60h           | $\text{NF}_4\text{Ti}_3\text{F}_{13}$ (2), $\text{NF}_4\text{BF}_4$ (1.4), $\text{NF}_3$ (2.6),<br>$\text{BF}_3$ (4.6)  |
| $\text{NF}_4\text{BF}_4$ (6), prefluor. $\text{TiF}_4$ (6)  | 170°, 20h           | $\text{NF}_4\text{Ti}_2\text{F}_9$ (5), $\text{NF}_4\text{BF}_4$ (3), $\text{BF}_3$ (3)   |
| $\text{NF}_4\text{BF}_4$ (6), prefluor. $\text{TiF}_4$ (12) | 170°, 20h           | $\text{NF}_4\text{Ti}_2\text{F}_9$ (5.6), $\text{NF}_4\text{Ti}_3\text{F}_{13}$ (1.6),<br>$\text{BF}_3$ (5.4), $\text{NF}_4\text{BF}_4$ (0.6)                           |
| $\text{NF}_4\text{BF}_4$ (6), prefluor. $\text{TiF}_4$ (12) | 170°, 192h          | $\text{NF}_4\text{Ti}_2\text{F}_9$ (6), $\text{BF}_3$ (6)   |

Table 2. X-Ray Powder Data for  $(\text{NF}_{4-2}\text{TiF}_6)^a$

| d obsd | d calcd | Int | h k l            |
|--------|---------|-----|------------------|
| 6.23   | 6.26    | vw  | 1 1 1            |
| 5.57   | 5.56    | vs  | 0 0 2            |
| 4.93   | 4.93    | w   | 1 0 2            |
| 3.49   | 3.50    | s   | 1 0 3            |
| 3.39   | 3.39    | s   | 3 1 0            |
| 2.94   | 2.93    | ms  | 2 1 3            |
| 2.782  | 2.778   | m   | 0 0 4            |
| 2.465  | 2.463   | w   | 3 3 1            |
| 2.315  | 2.318   | mw  | 3 2 3            |
| 2.201  | 2.200   | s   | 4 2 2            |
| 2.100  | 2.101   | w   | 5 1 0            |
| 1.990  | 1.990   | vw  | } 5 2 0<br>5 0 2 |
| 1.892  | 1.894   | m   |                  |
| 1.789  | 1.789   | mw  | } 6 0 0<br>4 4 2 |
| 1.663  | 1.664   | mw  |                  |
| 1.641  | 1.644   | mw  | 3 0 6            |

(a) tetragonal,  $a = 10.715\text{\AA}$ ,  $c = 11.114\text{\AA}$ , Cu  $K_\alpha$  radiation Ni filter



Table 3. Crystallographic Data of  $(\text{NF}_4)_2\text{TiF}_6$  Compared to Those of Other  $\text{NF}_4^+$  Salts

|                                 | Tetragonal Unit Cell Dimensions |                    |                      | Z    | Volume ( $\text{\AA}^3$ )<br>per F | Calcd Density<br>( $\text{g/cm}^3$ ) |
|---------------------------------|---------------------------------|--------------------|----------------------|------|------------------------------------|--------------------------------------|
|                                 | a ( $\text{\AA}$ )              | c ( $\text{\AA}$ ) | V ( $\text{\AA}^3$ ) |      |                                    |                                      |
| $\text{NF}_4\text{PF}_6^a$      | 7.577                           | 5.653              | 324.53               | 2    | 16.23                              | 2.41                                 |
| $\text{NF}_4\text{AsF}_6^b$     | 7.70                            | 5.73               | 339.73               | 2    | 16.99                              | 2.72                                 |
| $\text{NF}_4\text{SbF}_6^c$     | 7.903                           | 5.806              | 362.63               | 2    | 18.13                              | 2.98                                 |
| $\text{NF}_4\text{BiF}_6^c$     | 8.006                           | 5.821              | 373.10               | 2    | 18.66                              | 3.68                                 |
| $\text{NF}_4\text{BF}_4^a$      | 9.944                           | 5.229              | 517.04               | 4    | 16.16                              | 2.27                                 |
| $(\text{NF}_4)_2\text{GeF}_6^a$ | 10.627                          | 11.114             | 1255.14              | 16/3 | 16.81                              | 2.59                                 |
| $(\text{NF}_4)_2\text{SnF}_6^d$ | 10.828                          | 11.406             | 1337.35              | 16/3 | 17.91                              | 2.73                                 |
| $(\text{NF}_4)_2\text{TiF}_6$   | 10.715                          | 11.114             | 1276.01              | 16/3 | 17.09                              | 2.37                                 |

(a) Ref. 2

(b) Ref. 6

(c) Ref. 4

(d) Ref. 3

Table 4. Vibrational Spectra of Solid  $(\text{NF}_4)_2\text{TiF}_6$  Compared to Those of  $\text{Cs}_2\text{TiF}_6$

| obsd freq ( $\text{cm}^{-1}$ ) and rel intens <sup>a</sup> |           |       | assignments (point group) |   |
|--|-----------|-------|---------------------------|---|
| $(\text{NF}_4)_2\text{TiF}_6$                              |           |       | $\text{Cs}_2\text{TiF}_6$ | $\text{TiF}_6^{--}(\text{O}_h)^b$             |
| IR   | RA        | IR    | RA                        |   |
| 2340sh   |           |       |                           | $2\nu_3(\text{A}_1+\text{E}+\text{F}_2)$      |
| 2320vw   |           |       |                           | $\nu_1+\nu_3(\text{F}_2)$                     |
| 2003w  |           |       |                           | $\nu_3+\nu_4(\text{A}_1+\text{E}+\text{F}_2)$ |
| 1780sh   |           |       |                           | $\nu_1+\nu_4(\text{F}_2)$                     |
| 1760vw   |           |       |                           | $2\nu_4(\text{A}_1+\text{E}+\text{F}_2)$      |
| 1463w  |           |       |                           | $\nu_3(\text{F}_2)$                           |
| 1219mw   |           |       |                           | $\nu_2+\nu_4(\text{F}_1+\text{F}_2)$          |
| 1160vs   | 1158(1.4) |       |                           | $2\nu_2(\text{A}_1+\text{A}_2+\text{E})$      |
| 1132sh, vw   |           |       |                           | $\nu_1(\text{A}_1)$                           |
| 1060vw   |           |       |                           | $\nu_4(\text{F}_2)$                           |
| 1021w  |           |       |                           |   |
| 910vw  |           |       |                           | $\nu_1+\nu_4(\text{F}_{1u})$                  |
| 850sh, vw  | 883(0.1)  |       |                           |   |
| 804w   | 853(10)   |       |                           |   |
| 611mw  | 612(5)    |       |                           |   |
|  | 607sh     |       |                           |   |
|  | 601(8.0)  |       | 599(10)                   |   |
| 563vs  |           | 562vs |                           | $\nu_1(\text{A}_{1g})$                        |
| 452vw  | 450(3.3)  |       |                           | $\nu_3(\text{F}_{1u})$                        |
|  | 442(2.6)  |       |                           |   |
|  | 289(8.2)  |       |                           | $\nu_5(\text{F}_{2g})$                        |
|  | 107(0+)   |       |                           |   |
|  | 86(2)     |       |                           |   |
|  |           |       | 284(9.8)                  |   |
|  |           |       | 84(1.2)                   |   |
|  |           |       | 68(3.2)                   |   |
|  |           |       | 56(1.7)                   |   |
|  |           |       |                           | Lattice vibrations                            |

(a) uncorrected Raman intensities

(b) the site symmetry of  $\text{TiF}_6^{--}$  in  $\text{Cs}_2\text{TiF}_6$  is  $\text{D}_{3d}$ , but for simplicity and in view of the unknown site symmetry of  $\text{TiF}_6^{--}$  in  $(\text{NF}_4)_2\text{TiF}_6$ , the assignments for  $\text{TiF}_6^{--}$  were made for the point group  $(\text{O}_h)$  of the free ion.

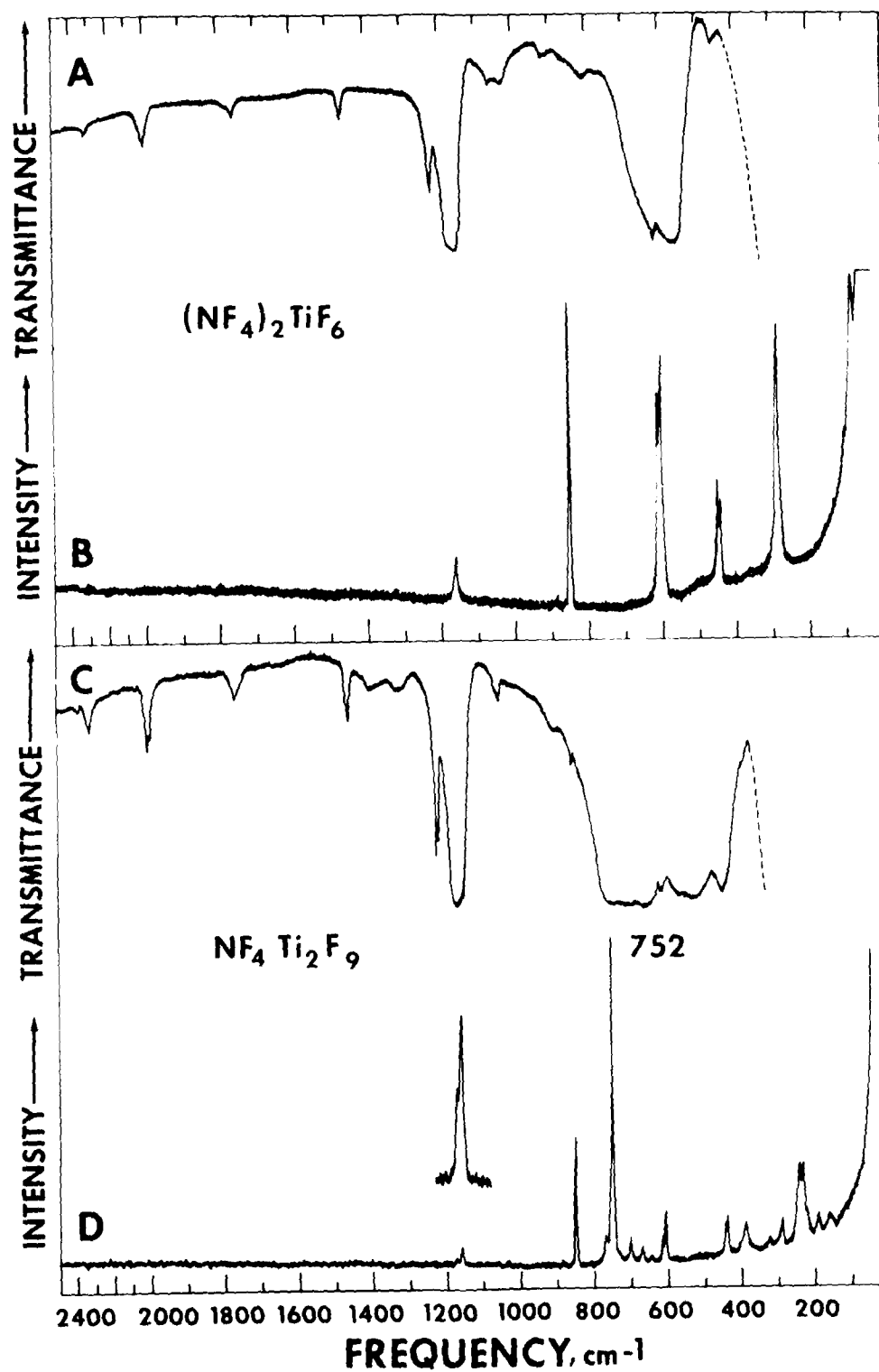


Table 6. Vibrational Spectra of Solid  $\text{Cs}_2\text{Ti}_2\text{F}_{10}$  and Prefluorinated  $\text{TiF}_4$

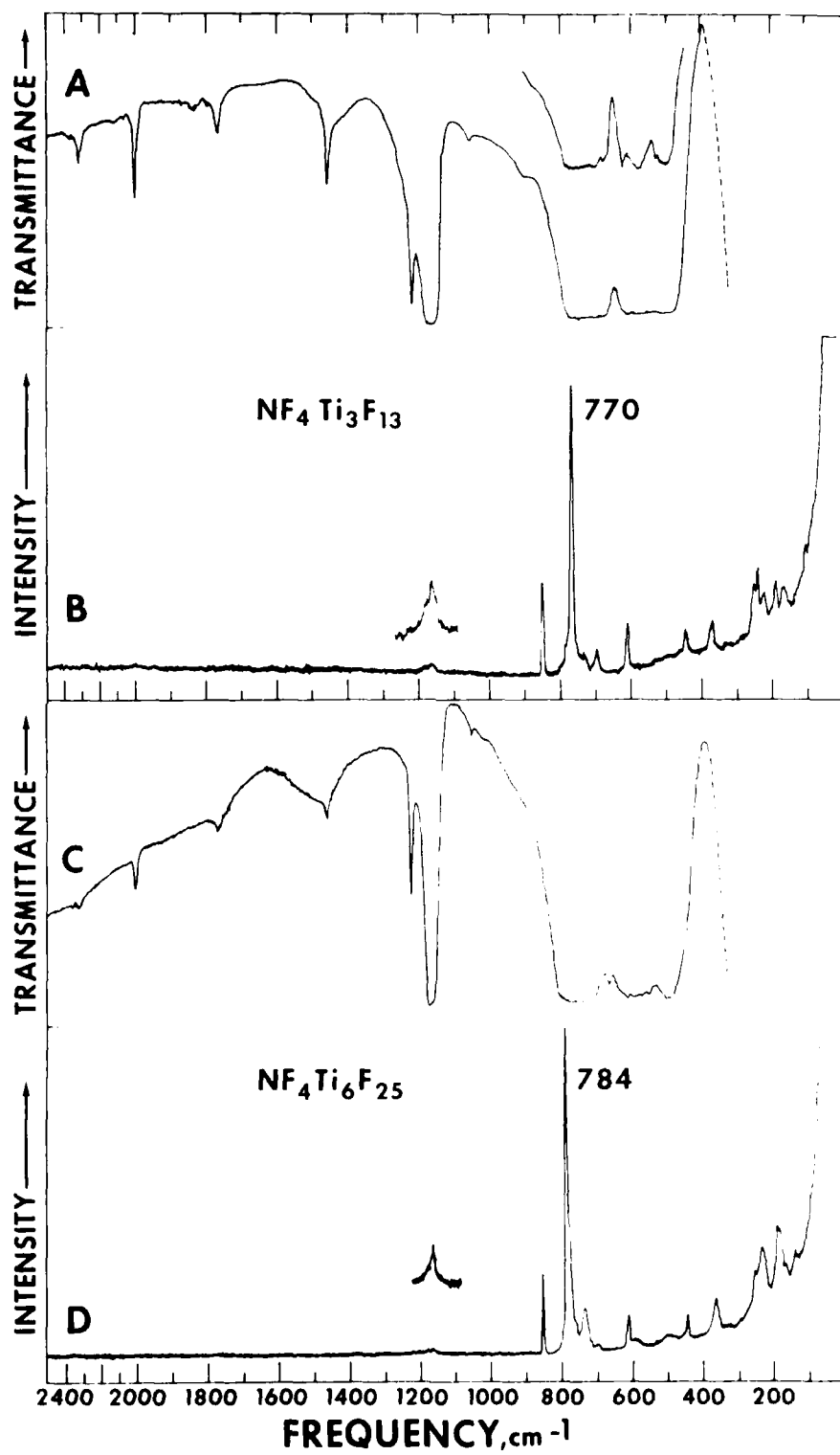
| $\text{Cs}_2\text{Ti}_2\text{F}_{10}$                      |  | $\text{TiF}_4$                        |   |
|--|--|---------------------------------------|---|
| obsd freq ( $\text{cm}^{-1}$ ) and rel intens <sup>a</sup> | assignments <sup>b</sup> for point group $D_{2h}$  | obsd freq and rel intens <sup>a</sup> |   |
| IR   | RA   | IR                                    | RA  |
| 730-600vs, br  | $\nu_1(\text{Ag})$<br>$\nu_{17}(\text{B}_{2g})$<br>$\nu_9(\text{B}_{1g})$<br>$\nu_2(\text{Ag})$  | 840-730vs, br                         | $\left\{ \begin{array}{l} 829(5.0) \\ 817(0.4) \end{array} \right\}$<br>$\left\{ \begin{array}{l} 807(10) \\ 761(1.7) \end{array} \right\}$<br>731(0.4) |
| 468m<br>441s   | $\nu_{13}(\text{B}_{1u})$<br>$\nu_{26}(\text{B}_{3u})$<br>$\nu_{20}(\text{B}_{2u})$<br>$\nu_{27}(\text{B}_{3u})$<br>$\nu_{28}(\text{B}_{3u})$<br>$\nu_{21}(\text{B}_{2u})$ | 580vs, br<br>481vs                    | 471(0.5)<br>370(1.7)<br>291(0.9)<br>239(1.8)<br>221(0+)   |
| 335(0.5)   | $\nu_{18}(\text{B}_{2g})$<br>$\nu_{11}(\text{B}_{1g})$   | 201(2.0)                              |   |
| 284(1.7)   | $\nu_4(\text{Ag})$   | 179(6.1)                              |   |
| 248(4.8)   | $\nu_{24}(\text{B}_{3g})$  | 140(2.0)                              |   |
| 218(2.8)   | $\nu_5(\text{Ag})$   | 99(0+)                                |   |
| 199(0.8)   | $\nu_{12}(\text{B}_{1g})$  | 87(0+)                                |   |
|  |  | 70(0+)                                |   |

(a) uncorrected Raman intensities

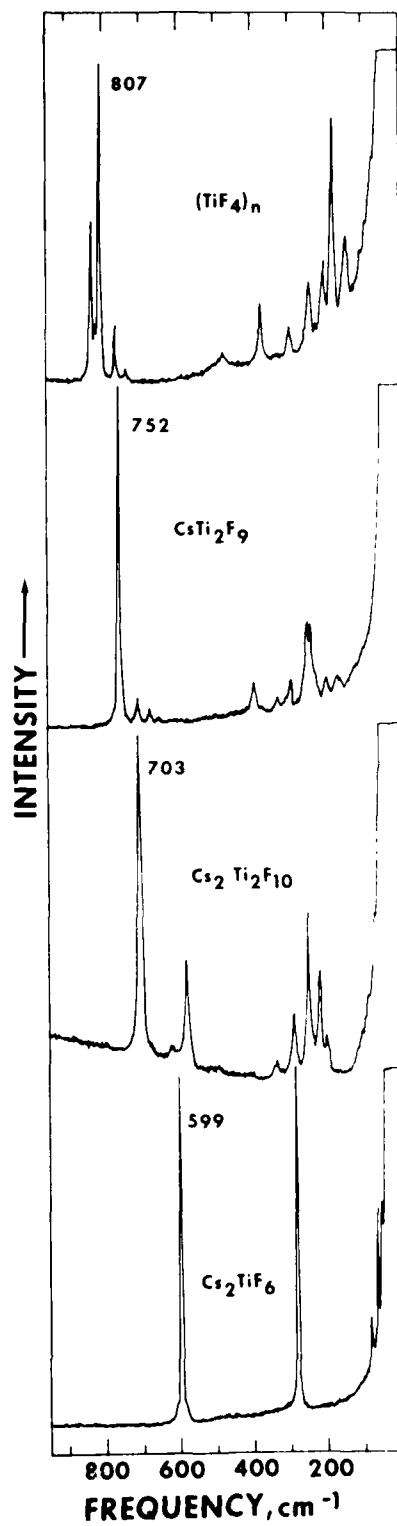
(b) using the symmetry co-ordinates of ref. 21



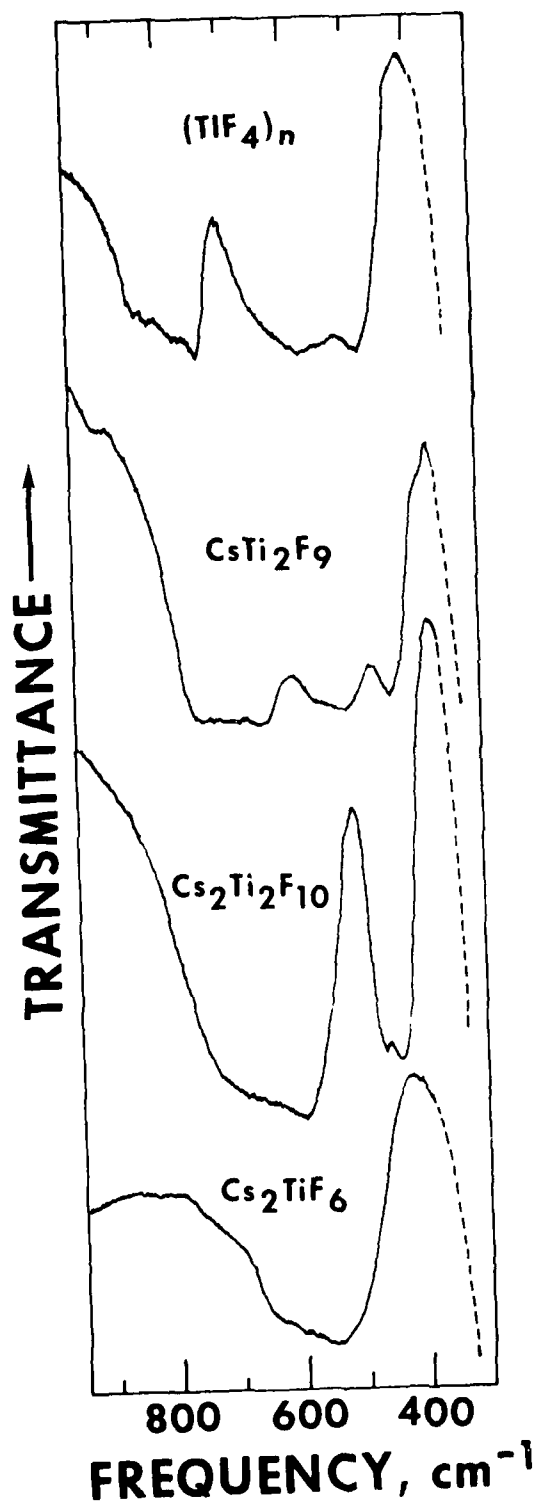
R-77-112  
G-22



R-77-112  
C-25



R-77-112  
C-24





Contribution from Rocketdyne, A Division of  
Rockwell International, Canoga Park, California 91304

Synthesis and Characterization of  $(\text{NF}_4)_2\text{NiF}_6$

Karl O. Christe

Received . . . . .

Abstract

The  $\text{NF}_4^+$  cation has successfully been coupled with the energetic  $\text{NiF}_6^{--}$  anion in the form of the stable  $(\text{NF}_4)_2\text{NiF}_6$  salt. The salt was prepared from  $\text{Cs}_2\text{NiF}_6$  and  $\text{NF}_4\text{SbF}_6$  by metathesis in  $\text{HF}$ . It was characterized by elemental analysis, vibrational spectroscopy, and its x-ray powder diffraction pattern. Its hydrolysis and thermal decomposition were studied.

Introduction

A large number of strongly oxidizing complex fluoro cations and anions are known. However, their potential application as energetic oxidizers had been handicapped by the fact that they formed stable salts only with nonenergetic counter ions. The recent syntheses<sup>1-3</sup> of several stable  $\text{NF}_4^+$  salts, derived from relatively weak Lewis acids, indicated that the  $\text{NF}_4^+$  cation might possess the necessary stability required for its successful combination with energetic anions.

In this paper we report the synthesis and properties of  $(\text{NF}_4)_2\text{NiF}_6$  which, to our knowledge, is the first known example of a stable salt containing both a strongly oxidizing complex fluoro cation and anion. The  $\text{NiF}_6^{--}$  anion is well known<sup>4-19</sup> and is a strong oxidizer owing to the fact that the parent molecule  $\text{NiF}_4$  is unstable and decomposes to lower nickel fluorides and elemental fluorine.<sup>17,18</sup>

### Experimental

Materials and Apparatus. The equipment and handling procedures used in this work were identical to those previously described.<sup>2,5</sup> The  $\text{NF}_4\text{SbF}_6$  was prepared as previously<sup>20</sup> reported. The HF (Matheson) was dried by  $\text{F}_2$  treatment<sup>22</sup> and was stored over  $\text{K}_2\text{NiF}_6$  (Ozark Mahoning) prior to use. The  $\text{Cs}_2\text{NiF}_6$  was prepared by heating a finely ground 2:1 molar mixture of dried CsF and  $\text{NiCl}_2$  (Alfa) with 15 mol of  $\text{F}_2$  per mol of  $\text{NiCl}_2$  in a nickel cylinder to 250°C for 16 hours. The volatile products were pumped off at room temperature. The solid product was finely powdered in the dry box and the fluorination step was repeated as described above. The weight and the vibrational spectra of the resulting crimson red solid were in excellent agreement with those expected<sup>9,15,16</sup> for  $\text{Cs}_2\text{NiF}_6$ .

In the infrared spectrum of  $\text{Cs}_2\text{NiF}_6$  several relatively intense previously unreported combination bands ( $\text{cm}^{-1}$ ) were observed. These were  $\nu_1+\nu_3$  (1205 w, 1187 mw),  $\nu_2+\nu_3$  (1164 mw, 1144 m),  $\nu_3+\nu_5$  (954 sh, 936 w),  $\nu_1+\nu_4$  (884 vw), and  $\nu_2+\nu_4$  (842 vw). From these combination bands a splitting

of  $\nu_3$  into two components with frequencies of 660 and 641  $\text{cm}^{-1}$  can be deduced. The observed frequencies ( $\text{cm}^{-1}$ ) and relative intensities of the fundamentals were: infrared,  $\nu_3$  (645 vs, br),  $\nu_4$  (331 s); Raman,  $\nu_1$  [545(10)],  $\nu_2$  [503(7.5)],  $\nu_5$  [294(4)].

Synthesis of  $(\text{NF}_4)_2\text{NiF}_6$ . In the glove box a mixture of  $\text{Cs}_2\text{NiF}_6$  (13.50 mmol) and  $\text{NF}_4\text{SbF}_6$  (27.94 mmol) was placed in a 3/4 inch o.d. Teflon FEP U-trap which was connected through a  $180^\circ$  coupling to a second U-trap. This coupling contained a porous Teflon filter (Pall Corporation). The free ends of both U-traps were closed off by valves. Both valves were connected through flexible, corrugated Teflon FEP tubing to a vacuum manifold. Dry HF (10 ml liquid) was added at  $-78^\circ\text{C}$  to the trap containing the reactants. The mixture was warmed to  $25^\circ\text{C}$  and stirred with a Teflon coated magnetic stirring bar for 30 minutes. The U-tube and filter coupling were cooled to  $-78^\circ\text{C}$  and the trap was inverted. The receiving trap was also cooled to  $-78^\circ\text{C}$  and the solution above the filter was pressurized by 2 atm of dry nitrogen to accelerate the filtration. After completion of the filtration, the HF solvent was removed by pumping for 12 hours at  $25^\circ\text{C}$ . The filter cake consisted of 10.15 g of a light brown solid (weight calcd for 27.0 mmol of  $\text{CsSbF}_6$  9.95 g) which was identified by analysis and vibrational spectroscopy as mainly  $\text{CsSbF}_6$  containing a small amount of  $\text{NF}_4^+$  and  $\text{NiF}_6^{--}$  salts. The filtrate residue consisted of 4.36 g of a deep red solid (weight calcd for 13.5 mmol of  $(\text{NF}_4)_2\text{NiF}_6$  4.76 g) which on the basis of elemental and spectroscopic analyses had the composition (weight %):  $(\text{NF}_4)_2\text{NiF}_6$ , 82.35;  $\text{NF}_4\text{SbF}_6$ , 13.98;  $\text{CsSbF}_6$ , 3.56.

Anal. Calcd: Ni, 13.71; Sb, 6.40; Cs, 1.28;  $\text{NF}_3$ , 36.20. Found: Ni, 13.70; Sb, 6.44; Cs, 1.31;  $\text{NF}_3$ , 36.19. The method for purifying this material by recrystallization from anhydrous HF at ambient temperature has previously been described<sup>20</sup> for  $\text{NF}_4\text{BF}_4$ .

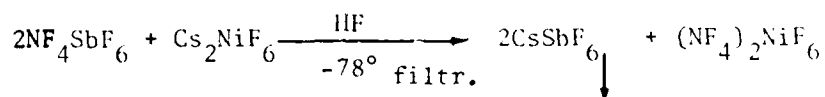
Hydrolysis of  $(\text{NF}_4)_2\text{NiF}_6$ . Caution! The reaction of  $(\text{NF}_4)_2\text{NiF}_6$  with water is very violent and can result in explosions. About 5 ml of distilled water was frozen out at  $-196^\circ$  in the upper section of a Teflon FEP U-trap containing about one mmol of  $(\text{NF}_4)_2\text{NiF}_6$ . The frozen water was knocked down into the bottom section of the tube containing the sample and the ice and sample were mixed by agitation at low temperature. After good mixing was achieved, the mixture was carefully warmed towards room temperature and as soon as interaction was noticeable, the mixture was chilled again by liquid  $\text{N}_2$ . This procedure was repeated until the color of the sample had completely changed from red to the green color characteristic for divalent nickel. The products volatile at  $-78^\circ\text{C}$  consisted of  $\text{O}_2$ ,  $\text{NF}_3$ , and  $\text{OF}_2$ . The oxygen was separated from the  $\text{NF}_3$  and  $\text{OF}_2$  at  $-210^\circ\text{C}$ , and the  $\text{NF}_3:\text{OF}_2$  ratio was determined by infrared spectroscopy. The hydrolysate was analyzed for Ni, Cs, and Sb by both x-ray fluorescence and atomic absorption spectroscopy. The mol ratio of  $\text{O}_2$  to  $\text{OF}_2$  was found to vary somewhat from experiment to experiment, but approached 2:1 with the total amount being close to that expected for the reduction of N(+V) and Ni(+IV) to N(+III) and Ni(+II), respectively. Control experiments on the hydrolysis of  $\text{Cs}_2\text{NiF}_6$  under identical conditions resulted in the evolution of  $\text{O}_2$  only in amounts corresponding to the reduction of Ni(+IV) to Ni(+II).

Pyrolysis of  $(\text{NF}_4)_2\text{NiF}_6$ . A sample of  $(\text{NF}_4)_2\text{NiF}_6$  (296 mg) was placed into a prepassivated (with  $\text{ClF}_3$ , followed by  $\text{F}_2$  at  $130^\circ\text{C}$ )  $1/4"$  o.d. stainless steel U-tube (volume 10.46 cc) closed off on both ends by Hoke valves (3132M25). One side of the U was connected to a pressure transducer (Validyne, Model AP10) and the other side to the vacuum line. The U-tube was kept at a constant temperature with an oil bath and the pressure build up was measured as a function of time. Periodic evacuation of the system revealed that the decomposition rate was not influenced by the pressure of the gaseous decomposition products. The decomposition rates of  $(\text{NF}_4)_2\text{NiF}_6$  were determined over the temperature range  $80$ - $128^\circ\text{C}$ . All measurements were carried out on one sample starting at the lowest temperature. At the highest temperature ( $128^\circ\text{C}$ ), an exhaustive pyrolysis of the remaining undecomposed 82% of the original sample was carried out until gas evolution practically ceased. The evolved gas was shown by infrared and mass spectroscopy to be a mixture of  $\text{NF}_3$  and  $\text{F}_2$  in a mole ratio of about 2:5. Based on its weight loss and vibrational spectrum, the solid residue from the exhaustive pyrolysis was shown to consist of the thermally more stable  $\text{NF}_4\text{SbF}_6$  and  $\text{CsSbF}_6$  impurities and the previously described<sup>9,17</sup> nonstoichiometric brown nickel fluoride  $\text{NiF}_{2.x}$ .

The thermal decomposition was also visually followed by heating a sample of  $(\text{NF}_4)_2\text{NiF}_6$  in a sealed glass capillary. At  $150^\circ\text{C}$  the color of the sample changed from dark red to brown ( $\text{NiF}_{2.x}$ ) which at higher temperatures changed to grey. Vibrational spectra of these decomposition products and those obtained from the yellow pyrolysis product of  $\text{Cs}_2\text{NiF}_6$  showed that in all cases the main product was  $\text{NiF}_2$  (Ra, 520 vs, 425 s, IR, 520 sh, 425 s, br).

## Results and Discussion

Synthesis and Properties. Since the  $\text{NiF}_6^{--}$  anion is stable in anhydrous HF solution<sup>9,12,17</sup>, the synthesis of  $(\text{NF}_4)_2\text{NiF}_6$  by metathesis appeared feasible. Both  $\text{NF}_4\text{SbF}_6$  and  $\text{Cs}_2\text{NiF}_6$  are highly soluble in HF, whereas  $\text{CsSbF}_6$  is of relatively low solubility, particularly at lower temperature. Consequently, the following reaction was used to prepare  $(\text{NF}_4)_2\text{NiF}_6$ :



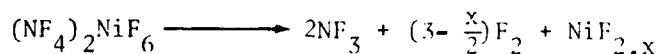
The optimization of a  $\text{NF}_4\text{SbF}_6$  - cesium salt based metathetical process and the possible product purification have previously been discussed in detail for the corresponding  $\text{NF}_4\text{BF}_4$  process<sup>20</sup>, and hence are not being reiterated.

The resulting  $(\text{NF}_4)_2\text{NiF}_6$  is a deep red hygroscopic solid, stable at room temperature. It crystallizes in the tetragonal system (see Table I) and is isotypic with the other known  $(\text{NF}_4)_2\text{MF}_6$  ( $\text{M}=\text{Ge}, \text{Sn}, \text{Ti}$ )<sup>1-3</sup> salts (see Table II). As expected, the size of the unit cell decreases from  $(\text{NF}_4)_2\text{TiF}_6$  to  $(\text{NF}_4)_2\text{NiF}_6$  owing to the transition metal contraction and then increases again when going from Ni to the main group elements.

The vibrational spectra of  $(\text{NF}_4)_2\text{NiF}_6$  are shown in Figure 1 and the observed frequencies and their assignments are summarized in Table III. The observed frequencies and intensities are in excellent agreement with those previously reported for other  $\text{NF}_4^+$  salts<sup>1-3</sup> and  $\text{K}_2\text{NiF}_6$ <sup>9,15</sup> and  $\text{Cs}_2\text{NiF}_6$  (see Experimental), thus establishing the ionic nature of  $(\text{NF}_4)_2\text{NiF}_6$ .

Thermal Decomposition. The thermal decomposition of  $(\text{NF}_4)_2\text{NiF}_6$  was investigated by DSC and visual observation of samples sealed in glass melting point capillaries. The DSC curves of samples sealed in aluminum pans indicated the onset of very slow endothermic decomposition between 110 and 120°C, which increased with increasing temperature and became rapid between 200 and 210°C. The fact that  $(\text{NF}_4)_2\text{NiF}_6$  undergoes appreciable decomposition well below 200°C was confirmed by visual observation of samples sealed in glass melting point capillaries. Heating to 130°C resulted in the formation of the brown nonstoichiometric  $\text{NiF}_{2.x}^{9,17}$  (see Experimental). As previously discussed,<sup>1-3</sup> these data are only qualitative.

Since the thermal stability of a powerful oxidizer, such as  $(\text{NF}_4)_2\text{NiF}_6$ , is of great practical importance, its rate of decomposition was quantitatively studied by total pressure measurements over the temperature range 80 to 128°C. The decomposition follows the equation:



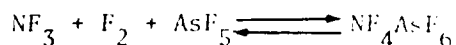
The decomposition rate was found to be independent of the gas pressure, as expected for an irreversible reaction involving the decomposition of the thermodynamically unstable  $\text{NiF}_4$  to  $\text{NiF}_{2.x}$ . Owing to the limited amount of sample available, all measurements were carried out on the same sample. From 80 to 110°C the decomposition rates were measured only for low  $\alpha$  (fraction of material decomposed) values. At 128°C an exhaustive decomposition was carried out (see Figure 2) for the  $\alpha$  range 0.18 to 1. Plots of  $\alpha$  as a function of time  $t$  resulted in straight lines for the  $\alpha$  range 0-0.18 from 80 to 110°C and for  $\alpha$  0.18-0.6 at 128°C. From these straight lines, rate constants,  $k$ , were

calculated for each temperature (see Table IV). An Arrhenius plot of  $\log k$  versus  $\frac{1}{T}$  resulted in a straight line. The fact that this plot included the data points obtained for both low and high  $\alpha$  values strongly suggests that the decomposition rates are independent of  $\alpha$  at  $\alpha < 0.6$ . From the Arrhenius plot, the following expressions can be derived for the specific reaction rate constant ( $\text{sec}^{-1}$ ) and activation energy of the  $(\text{NF}_4)_2\text{NiF}_6$  decomposition:

$$k = 4.840 \cdot 10^{14} \cdot e^{-\frac{35161}{RT(^{\circ}\text{K})}} \quad \text{and } \Delta H_a = 35.161 \text{ kcal/mol}$$

A detailed study of the exact decomposition mechanism was beyond the scope of this study. However, the failure to observe significant sigmoid character for the decomposition curves indicates that the decomposition is not autocatalytic. Furthermore, the fact that the decomposition rates were independent of  $\alpha$  over a large range of  $\alpha$  suggests that the decomposition occurs at active sites and that the number of these sites is fixed.<sup>22</sup>

The thermal decomposition of  $(\text{NF}_4)_2\text{NiF}_6$  strongly differs from that previously reported<sup>23</sup> for  $\text{NF}_4\text{AsF}_6$ . Contrary to our findings for  $(\text{NF}_4)_2\text{NiF}_6$ , the decomposition of  $\text{NF}_4\text{AsF}_6$  was found to be pressure dependent indicating the equilibrium:

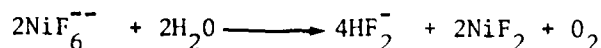


Because of the irreversibility of the  $(\text{NF}_4)_2\text{NiF}_6$  decomposition, the heat of dissociation and thereby the heat of formation of solid  $(\text{NF}_4)_2\text{NiF}_6$  cannot be computed. However, in view of its importance for performance calculations, the heat of formation of solid  $(\text{NF}_4)_2\text{NiF}_6$  was estimated to be about -230 kcal/mol based on the following sequence:

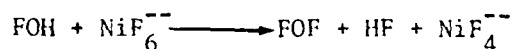
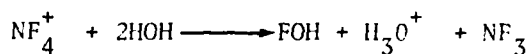




which, in agreement with a previous report<sup>9</sup>, produced only  $O_2$  according to:



The hydrolysis of  $NF_4^+$  salts containing nonoxidizing anions have previously been studied. Although  $O_2$  evolution had not always been quantitative,  $H_2O_2$  and not  $OF_2$  had been the only observed by-product<sup>3</sup>. It thus appears that the combination of  $NF_4^+$  and  $NiF_6^{--}$  are required to produce significant amounts of  $OF_2$ . A plausible explanation for the formation of  $OF_2$  is the fluorination of  $HO\dot{F}$ , a likely intermediate in the rapid hydrolysis of  $NF_4^+$ ,<sup>3</sup> by the hydrolytically more stable  $NiF_6^{--}$  according to:



Summary. The successful synthesis of  $(NF_4)_2NiF_6$  is significant since, to our knowledge, it is the first combination of a strongly oxidizing complex fluoro cation with a strongly oxidizing complex fluoro anion in the form of a stable salt. Its potential as an oxidizer becomes evident from the following comparison. On thermal decomposition, one  $cm^3$  of solid  $(NF_4)_2NiF_6$  is capable of producing 1.5 times as much useful fluorine, i.e. in the form of  $F_2$  and  $NF_3$ , as liquid  $F_2$  at  $-187^\circ C$ . Furthermore,  $(NF_4)_2NiF_6$  is a stable solid at ambient temperature which can be safely stored without requiring cryogenic cooling. The physical and spectroscopic properties of  $(NF_4)_2NiF_6$  are in excellent agreement with those predicted for a solid containing  $NF_4^+$  and  $NiF_6^{--}$  ions. The only unexpected property was the observation of significant

amounts of  $\text{OF}_2$  during hydrolysis.

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Diagram Captions

Figure 1. - Vibrational spectra of solid  $(\text{NF}_4)_2\text{NiF}_6$ . Trace A, infrared spectrum of the dry powder in a silver chloride disk, the absorption below  $400\text{ cm}^{-1}$  (broken line) being due to the AgCl windows. Trace B, Raman spectrum, recorded on a Cary Model 83 using the  $6471\text{Å}$  line of a Kr ion laser and a spectral slitwidth of  $2\text{ cm}^{-1}$ .

Figure 2. - Thermal decomposition curve of  $(\text{NF}_4)_2\text{NiF}_6$  measured at  $128^\circ\text{C}$ .

Table 1. X-Ray Powder Data for  $(\text{NF}_4)_2\text{NiF}_6^{\text{a}}$

| d obsd | d calcd | Int | h k l            |
|--------|---------|-----|------------------|
| 5.46   | 5.49    | vs  | 0 0 2            |
| 3.42   | 3.45    | ms  | 1 0 3            |
| 3.31   | 3.31    | s   | 3 1 0            |
| 2.880  | 2.878   | ms  | 2 1 3            |
| 2.742  | 2.738   | mw  | 0 0 4            |
| 2.407  | 2.405   | mw  | 3 3 1            |
| 2.150  | 2.150   | s   | 4 2 2            |
| 1.954  | 1.954   | w   | { 5 0 2<br>4 3 2 |
| 1.846  | 1.849   | m   | 4 4 0            |

(a) tetragonal,  $a = 10.457\text{\AA}$ ,  $c = 10.953\text{\AA}$ ,  $\text{CuK}_{\alpha}$  radiation Ni filter

Table 2. Crystallographic Data of  $(\text{NF}_4)_2\text{NiF}_6$  Compared to Those of Other  $(\text{NF}_4)_2\text{MF}_6$  Salts<sup>a</sup>

|  | Tetragonal Unit Cell Dimensions |        |                      | Volume ( $\text{\AA}^3$ )<br>per F | Calcd Density<br>( $\text{g/cm}^3$ ) |
|--|---------------------------------|--------|----------------------|------------------------------------|--------------------------------------|
|  | a (Å)                           | c (Å)  | V ( $\text{\AA}^3$ ) |                                    |                                      |
| $(\text{NF}_4)_2\text{TiF}_6^{\text{b}}$ | 10.715                          | 11.114 | 1276.0               | 17.09                              | 2.57                                 |
| $(\text{NF}_4)_2\text{NiF}_6$            | 10.457                          | 10.953 | 1197.7               | 16.04                              | 2.61                                 |
| $(\text{NF}_4)_2\text{GeF}_6^{\text{c}}$ | 10.627                          | 11.114 | 1255.1               | 16.81                              | 2.59                                 |
| $(\text{NF}_4)_2\text{SnF}_6^{\text{d}}$ | 10.828                          | 11.406 | 1337.4               | 17.91                              | 2.73                                 |

(a) For all compounds  $Z = 16/3$

(b) Ref. 1

(c) Ref. 3

(d) Ref. 2

Table 3. Vibrational Spectra of Solid  $(\text{NF}_4)_2\text{NiF}_6$

— obsd freq ( $\text{cm}^{-1}$ ) and rel intens<sup>a</sup> — — assignments (point group)<sup>b</sup> —

| IR                  | RA                                  | $\text{NF}_4^+$ ( $T_d$ ) | $\text{NiF}_6^{--}$ ( $O_h$ ) |
|---------------------|-------------------------------------|---------------------------|-------------------------------|
| 2301 vw             |                                     | $2\nu_3(A_1+E+F_2)$       |                               |
| 1998 w              |                                     | $\nu_1+\nu_3(F_2)$        |                               |
| 1756 vw             |                                     | $\nu_3+\nu_4(A_2+E+F_2)$  |                               |
| 1460 vw             |                                     | $\nu_1+\nu_4(F_2)$        |                               |
| 1218 m              |                                     | $2\nu_4(A_1+E+F_2)$       |                               |
| 1156 vs             | 1157 (0.1)                          | $\nu_3(F_2)$              |                               |
| 1055 vw             |                                     | $\nu_2+\nu_4(F_1+F_2)$    |                               |
| 854 vw              | 854 (1)                             | $\nu_1(A_1)$              |                               |
| 648 vs              |                                     |                           | $\nu_3(F_{1u})$               |
| 609 m }<br>604 sh } | 609 (0.5)                           | $\nu_4(F_2)$              |                               |
| 556 vw              | 555 (10)                            |                           | $\nu_1(A_{1g})$               |
| 512 vw              | 512 (7)<br>457 (0.5)<br>454 (0.5) } | $\nu_2(E)$                | $\nu_2(E_g)$                  |
| 443 vw              |                                     |                           |                               |
| 332 mw              |                                     |                           | $\nu_4(F_{1u})$               |
|                     | 307 (1.5) }<br>298 (4) }            |                           | $\nu_5(F_{2g})$               |
|                     | 90 (0.1) }<br>60 (0+) }             | LATTICE VIBRATIONS        |                               |

(a) uncorrected Raman intensities

(b) the actual site symmetries of  $\text{NF}_4^+$  and  $\text{NiF}_6^{--}$  in this salt are probably lower than  $T_d$  and  $O_h$ , respectively, as indicated by the large unit cell ( $Z = 16/3$ ) and the observed slight deviations from the selection rules and the lifting of the degeneracy for some of the modes; however, since the actual site symmetries are unknown, the assignments are given for the idealized point groups.

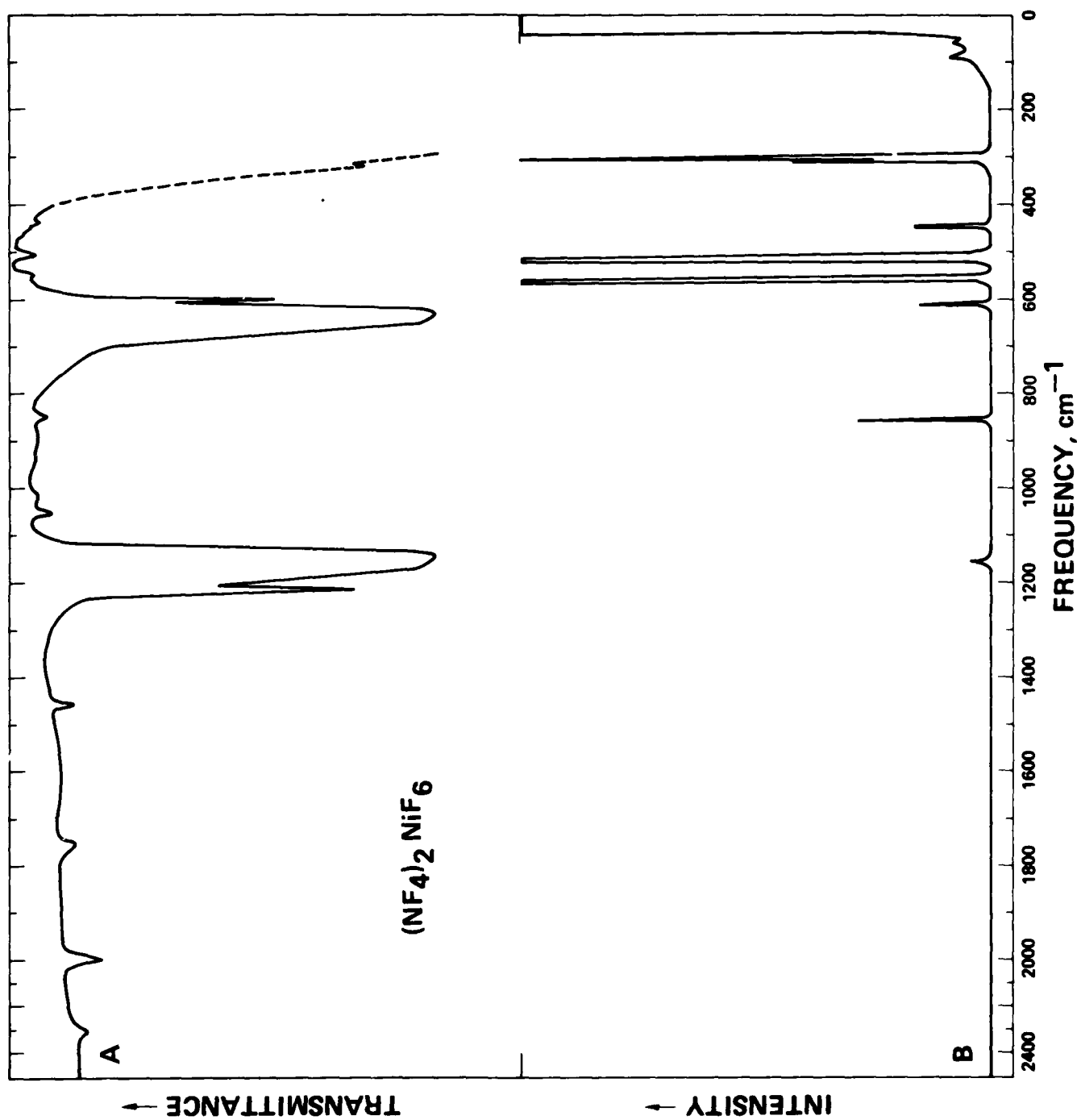
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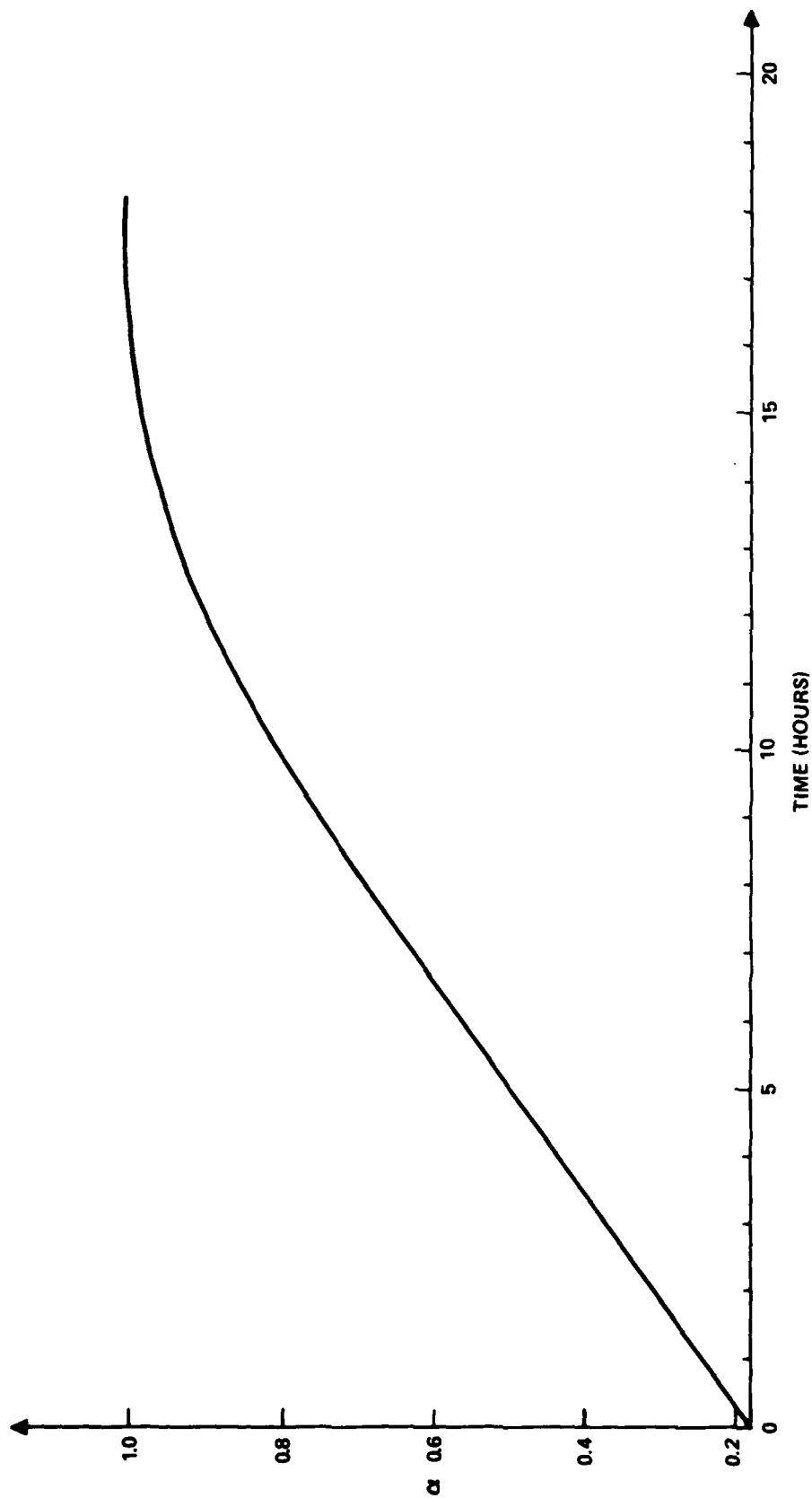


Table 4. Rate Constants Observed for the Thermal Decomposition  
of  $(\text{NF}_4)_2\text{NiF}_6$

| T (°C) | k (sec <sup>-1</sup> ) |
|--------|------------------------|
| 80     | $8.279 \cdot 10^{-8}$  |
| 90     | $2.739 \cdot 10^{-7}$  |
| 99     | $1.165 \cdot 10^{-6}$  |
| 110    | $4.197 \cdot 10^{-6}$  |
| 128    | $3.012 \cdot 10^{-5}$  |



R-77-112  
D-18



R-77-112  
D-19

## Vibrational spectrum and normal coordinate analysis of SF<sub>3</sub>Br

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**Abstract**—The i.r. spectrum of gaseous and the Raman spectrum of liquid SF<sub>3</sub>Br are reported. Ten out of 11 fundamentals expected for symmetry C<sub>4v</sub> were observed and assigned. A normal coordinate analysis was carried out and thermodynamic properties in the range 0–2000 K were computed.

### INTRODUCTION

Whereas the vibrational spectra and force fields of SF<sub>3</sub>Cl [1–3], SeF<sub>3</sub>Cl [4], and TeF<sub>3</sub>Cl [5] have been well characterized, similar data on the corresponding bromine compounds are lacking. Since SF<sub>3</sub>Br is an important intermediate for the synthesis of SF<sub>6</sub> substituted compounds, a thorough characterization of this molecule was desired. In this paper, we report its vibrational spectrum and the results of a normal coordinate analysis.

### EXPERIMENTAL

The SF<sub>3</sub>Br was prepared by the interaction of BrF with SF<sub>4</sub> in the presence of CsF in a stainless steel reactor at 90° for 24 hr. The reaction products were separated by repeated fractional condensation through a series of traps maintained at –95 and –112°. The SF<sub>3</sub>Br was retained in the –112° trap. It was found difficult to obtain a colorless product, free of traces of Br<sub>2</sub>, owing to its tendency to decompose to S<sub>2</sub>F<sub>10</sub> and Br<sub>2</sub> under the influence of light.

The i.r. spectra were recorded at Rocketdyne on both a Perkin–Elmer Model 457 and a Beckman Model 4250 spectrophotometer, calibrated by comparison with standard calibration points [6]. Stainless steel cells of 5 and 10-cm path length fitted with AgCl or high density polyethylene windows (seasoned with ClF<sub>3</sub>) were used as sample containers. The Raman spectrum of liquid SF<sub>3</sub>Br was recorded at UC Berkeley on a Spex Model 1400 double monochromator, using the 6764 Å exciting line for a Kr ion laser and quartz capillaries as sample containers.

### RESULTS AND DISCUSSION

#### *Vibrational spectra of SF<sub>3</sub>Br.*

The i.r. spectrum of SF<sub>3</sub>Br is shown in Fig. 1. Three very weak bands at 945, 820 and 545 cm<sup>–1</sup> were deleted from the figure, since their relative intensities varied from sample to sample and bands of similar frequencies have previously been reported [7] for S<sub>2</sub>F<sub>10</sub>, the photolytic decomposition product of SF<sub>3</sub>Br. The frequencies observed for the i.r. spectrum of the gas and the Raman spectrum of the liquid, together with their assignments for point group C<sub>4v</sub>, are given in Table 1. The agreement between the frequencies of the gas and the liquid is good indicating very little or no association in the liquid phase.

Since SF<sub>3</sub>Br can be considered as a monosubstituted derivative of octahedral SF<sub>6</sub>, it should belong to point group C<sub>4v</sub>. The 11 fundamentals of SF<sub>3</sub>Br of symmetry C<sub>4v</sub> can be classified as 4A<sub>1</sub> + 2B<sub>1</sub> + B<sub>2</sub> + 4E. Of these, all 11 modes should be Raman active, whereas only the A<sub>1</sub> and E modes should be i.r. active. Of the Raman lines, only the four A<sub>1</sub> modes should be polarized.

The observed spectrum agrees with these predictions. The assignment of the bands to the individual modes was done by analogy with the known spectra of closely related SF<sub>3</sub>Cl [1–3], SeF<sub>3</sub>Cl [4], and SF<sub>3</sub>O [8] (see Table 2) and, therefore, requires only little discussion. For SF<sub>3</sub>Cl the revised assignment [4] was used. The frequencies of SF<sub>3</sub>Br, which mainly involve motions of the SF<sub>3</sub> part of the molecule, deviate by less than 24 cm<sup>–1</sup> from those previously reported for SF<sub>3</sub>Cl [1–3]. The vibrations involving mainly an S–Br motion show the expected pronounced mass effect. The frequency of

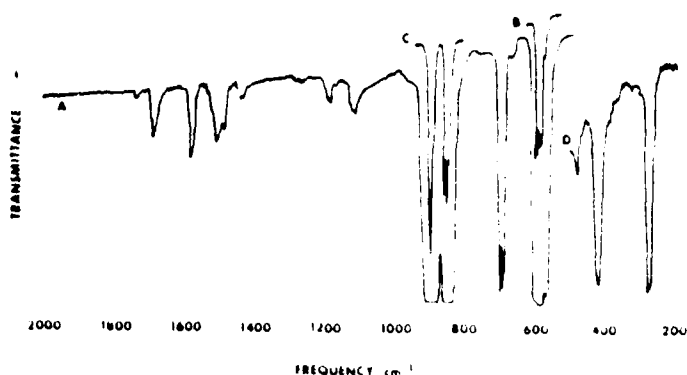


Fig. 1. Infrared spectrum of gaseous  $\text{SF}_4\text{Br}$ . Traces A, B and C, 100, 4.5 and 1 mm, respectively, in a 5 cm pathlength cell with  $\text{AgCl}$  windows; trace D, 700 mm in a 10 cm pathlength cell with polyethylene windows.

$275\text{ cm}^{-1}$  assigned to the S-Br stretch in  $\text{SF}_4\text{Br}$  is in good agreement with the value of  $305\text{ cm}^{-1}$  found for this mode in  $\text{BrSO}_2\text{F}$  [9].

The above assignments are further supported by the observed i.r. band contours (PQR structure for the  $A_1$  modes), the Raman polarization data, and the fact that all the observed combination bands (see Table I) can be assigned without violation of

the  $C_{4v}$  selection rules. The failure to detect  $\nu_7$  in the Raman spectrum is no surprise since for this type of molecules this mode is generally of very low intensity and also was not observed for the related molecules  $\text{SF}_4\text{Cl}$  [1-3] and  $\text{SeF}_4\text{Cl}$  [5]. By analogy with  $\text{SF}_4\text{Cl}$  [3],  $\nu_{11}$  of  $\text{SF}_4\text{Br}$  is of very low intensity in the i.r. spectrum, but is readily observed in the Raman spectrum.

Table I. Vibrational spectra of  $\text{SF}_4\text{Br}$  and their assignment in point group  $C_{4v}$ .

| Obsd freq. $\text{cm}^{-1}$ , and intensity* |                 |   |
|--|-----------------|---|
| Infrared<br>gas                              | Raman<br>liquid | Assignment  |
| 1745 vw                                      |                 | $\nu_1 + \nu_8 = 1743 (E)$                                  |
| 1696 w                                       |                 | $2\nu_1 = 1698 (A_1)$                                       |
| 1588 w                                       |                 | $\nu_2 + \nu_8 = 1586 (E)$                                  |
| 1540 vw                                      |                 | $\nu_1 + \nu_2 = 1541 (A_1)$                                |
| 1514 w                                       |                 | $\nu_8 + \nu_8 = 1514 (E)$                                  |
| 1489 vw                                      |                 | $\nu_3 + \nu_8 = 1485 (E)$                                  |
| 1443 vw                                      |                 | $\nu_1 + \nu_3 = 1440 (A_1)$                                |
| 1280 vw                                      |                 | $\nu_2 + \nu_3 = 1283 (A_1)$                                |
| 1268 vw                                      |                 | $\nu_1 + \nu_{10} = 1267 (E)$ or $\nu_2 + \nu_9 = 1267 (E)$ |
| 1193 vw                                      |                 | $\nu_8 + \nu_9 = 1195 (E)$                                  |
| 1175 vvw                                     |                 | $2\nu_3 = 1182 (A_1)$                                       |
| 1120 vw                                      |                 | $\nu_1 + \nu_4 = 1120 (A_1)$                                |
| 894 vs                                       | 898 (0.2) dp    | $\nu_8 (E)$   |
| 849 vs, P, Q, R                              | 848 (0.02) p    | $\nu_1 (A_1)$   |
| 692 m, P, Q, R                               | 691 (7.6) p     | $\nu_2 (A_1)$   |
|  | 620 (0.3) dp    | $\nu_8 (B_1)$   |
| 591 m, P, Q, R                               | 586 (0.2) p     | $\nu_3 (A_1)$   |
| 575 m  | 575 (0.02) dp   | $\nu_9 (E)$   |
|  | 500 (0.2) dp    | $\nu_7 (B_2)$   |
| 477 vw                                       |                 | $\nu_2 + \nu_{11} = 470 (E)$                                |
| 418 mw                                       | 419 (0.4) dp    | $\nu_{10} (E)$  |
| 271 mw                                       | 272 (10) p      | $\nu_4 (A_1)$   |
|  | 222 (0.6) dp    | $\nu_{11} (E)$  |

\* Uncorrected Raman intensities

# Vibrational spectrum and normal coordinate analysis of SF<sub>5</sub>Br

Table 2. Vibrational spectrum of SF<sub>5</sub>Br compared to those of SF<sub>5</sub>Cl, SF<sub>5</sub>O, and SeF<sub>5</sub>Cl

| Obsd freq, cm <sup>-1</sup> , and intensity |               |                          |              |                       |           |                         |              |   |  |
|---|---------------|--------------------------|--------------|-----------------------|-----------|-------------------------|--------------|---|--|
| SF <sub>5</sub> Br                          |               | SF <sub>5</sub> Cl [1-4] |              | SF <sub>5</sub> O [8] |           | SeF <sub>5</sub> Cl [4] |              | Assignment in point group C <sub>4v</sub> | Approximate description of vibration   |
| i.r. gas                                    | Ra liquid     | i.r. gas                 | Ra liquid    | i.r.                  | Ra        | i.r. gas                | Ra liquid    |   |  |
| 849 vs                                      | 848 (0.02) p  | 855 vs                   | 833 (0.2) p  | 735 vs                | 722 (0.2) | 729 ms                  | 721 (1.8) p  | A <sub>1</sub> ν <sub>1</sub>             | ν (XF <sub>5</sub> )                   |
| 692 m                                       | 691 (7.6) p   | 707 s                    | 704 (3) p    | 697 m                 | 697 (10)  | 654 w                   | 656 (10) p   | ν <sub>2</sub>                            | ν sym (XF <sub>4</sub> )               |
| 591 m                                       | 586 (0.2) p   | 602 s                    | 603 (0.2) p  | 506 s                 | 506 (1)   | 440 vs                  | 443 (2.2) p  | ν <sub>3</sub>                            | δ sym out of plane (XF <sub>4</sub> )  |
| 271 mw                                      | 272 (10) p    | 402 s                    | 403 (10) p   | 1154 vs               | 1153 (1)  | 384 mw                  | 385 (8.5) p  | ν <sub>4</sub>                            | ν (XY)                                 |
|   | 620 (0.3) dp  |                          | 625 (0.7) dp |                       | 541 (3.3) |                         | 646 (0.6) dp | B <sub>1</sub> ν <sub>5</sub>             | ν sym out of phase (XF <sub>4</sub> )  |
|   |               |                          |              |                       | 472 (0.2) |                         |              | ν <sub>6</sub>                            | δ asym out of plane (XF <sub>4</sub> ) |
|   | 500 (0.2) dp  |                          | 505 (0.2) dp |                       | 452 (0.9) |                         | 380 dp       | B <sub>2</sub> ν <sub>7</sub>             | δ sym in plane (XF <sub>4</sub> )      |
| 894 vs                                      | 898 (0.2) dp  | 909 vs                   | 927 (0.2) dp | 785 vs                | 780 (0.1) | 745 vs                  | 745 (0.3) dp | E ν <sub>8</sub>                          | ν asym (XF <sub>4</sub> )              |
| 575 m                                       | 575 (0.02) dp | 579 mw                   | 584 (0.1) dp | 530 sh                | 530 (2)   | 421 s                   | 424 (0.4) dp | ν <sub>9</sub>                            | δ (F <sub>2</sub> XF <sub>4</sub> )    |
| 418 mw                                      | 419 (0.4) dp  | 441 m                    | 442 (0.8) dp | 325 mw                |           | 334 m                   | 336 (1.2) dp | ν <sub>10</sub>                           | δ asym in plane (XF <sub>4</sub> )     |
|   | 222 (0.6) dp  | 287 vw                   | 271 (0.6) dp | 606 s                 | 607 (2.2) |                         | 213 (1.4) dp | ν <sub>11</sub>                           | δ (YXF <sub>4</sub> )                  |

## Force constants

A normal-coordinate analysis was carried out to aid the spectral assignment. The kinetic and potential energy metrics were computed by a machine method [10], assuming the following geometry and coordinate definitions:  $R_{\text{SF}_5} = r_{\text{SF}_5} = 1.60 \text{ \AA}$ ,  $D_{\text{SF}_5} = 2.27 \text{ \AA}$  [11],  $\alpha = \angle \text{FSF} = 90^\circ$ ,  $\beta = \angle \text{FSF}' = 90^\circ$  and  $\gamma = \angle \text{BrSF} = 90^\circ$ , where F' refers to the axial (unique) fluorine ligand. The symmetry coordinates used were identical with those previously reported [12] for IF<sub>5</sub>O. The deformation coordinates were weighted by unit (1 Å) distance.

The force constants were calculated by trial and error with the aid of a computer to give an exact fit between the observed and computed frequencies using the simplest possible modified valence force

field. Unique force constants could not be computed since the general valence force field has 24 symmetry force constants and there are only 11 frequencies. It was found that in both the A<sub>1</sub> and E block off-diagonal force constants are required to fit the observed frequencies. In the A<sub>1</sub> block, the  $F_{12}$ ,  $F_{23}$ , and  $F_{24}$  terms may be neglected [13] since their corresponding G matrix elements are zero. In the E block, however, all G matrix elements are nonzero. Based on our experience with related molecules, the most plausible interaction constants were selected and their values were kept as small as possible. Additional criteria for selecting the off-diagonal F terms were a plausible potential energy distribution and the condition to make  $F_{11} = f_{\text{F}} = f$ . The resulting force constants are listed in Tables 3 and 4. Uncertainty estimates are difficult to make

Table 3. Symmetry force constants of SF<sub>5</sub>Br\*

|                               |        |  |         |
|-------------------------------|--------|--|---------|
| A <sub>1</sub> ν <sub>1</sub> | 849    | $F_{11} = f_{\text{F}}$  | = 4.50  |
| ν <sub>2</sub>                | 692    | $F_{22} = f_{\text{F}} + 2f_{\text{FF}} + f_{\text{FF}}'$  | = 5.36  |
| ν <sub>3</sub>                | 591    | $F_{33} = \frac{1}{2}(f_{\text{F}} + 2f_{\text{FF}} + f_{\text{FF}}' + f_{\text{F}} + \phi_{\text{F}} + f_{\text{FF}}' - 2f_{\text{FF}} + 4f_{\text{FF}} - 2f_{\text{FF}}')$ | = 2.35  |
| ν <sub>4</sub>                | 271    | $F_{44} = f_{\text{F}}$  | = 2.23  |
|                               |        | $F_{14} = \sqrt{2}(f_{\text{FF}} - f_{\text{FF}}')$  | = 0.48  |
|                               |        | $F_{14} = f_{\text{FF}}$   | = 0.67  |
|                               |        | $F_{14} = \sqrt{2}(f_{\text{FF}} - f_{\text{FF}}')$  | = -0.30 |
| B <sub>1</sub> ν <sub>5</sub> | 620    | $F_{55} = f_{\text{F}} - 2f_{\text{FF}} + f_{\text{FF}}'$  | = 4.30  |
| ν <sub>6</sub>                | [470]† | $F_{66} = \frac{1}{2}(f_{\text{F}} - 2f_{\text{FF}} + f_{\text{FF}}' + f_{\text{F}} - 2f_{\text{FF}} + f_{\text{FF}}' - 2f_{\text{FF}} + 4f_{\text{FF}} - 2f_{\text{FF}}')$  | = 3.16  |
| B <sub>2</sub> ν <sub>7</sub> | 500    | $F_{77} = f_{\text{F}} - 2f_{\text{FF}} + f_{\text{FF}}'$  | = 1.79  |
| E ν <sub>8</sub>              | 894    | $F_{88} = f_{\text{F}} - f_{\text{FF}}'$   | = 3.74  |
| ν <sub>9</sub>                | 575    | $F_{99} = f_{\text{F}} - f_{\text{FF}}'$   | = 2.62  |
| ν <sub>10</sub>               | 418    | $F_{1010} = f_{\text{F}} - f_{\text{FF}}'$   | = 1.90  |
| ν <sub>11</sub>               | 222    | $F_{1111} = f_{\text{F}} - f_{\text{FF}}'$   | = 1.26  |
|                               |        | $F_{2020} = f_{\text{FF}} - f_{\text{FF}}'$  | = 0.66  |
|                               |        | $F_{2020} = f_{\text{FF}} - f_{\text{FF}}'$  | = 0.45  |

\* Stretching constants in mdyne/Å, deformation constants in mdyne/Å<sup>2</sup>, and stretch-bend interaction constants in mdyne/radian.  
† Estimated value.

Table 4. Internal force constants of SF<sub>6</sub>Bz<sup>a†</sup>

|                                     |  |
|-------------------------------------|--|
| $f_N = 4.50$                        | $f_{\mu\mu'} = 0.596$                  |
| $f_D = 2.23$                        | $f_{\gamma} = 1.479$                   |
| $f_r = 4.285$                       | $f_{r\gamma} = -0.128$                 |
| $f_{\pi} = 0.265$                   | $f_{r\gamma} = 0.219$                  |
| $f_{\pi'} = 0.545$                  | $f_{\mu\mu} = 0.34$                    |
| $f_{\mu\lambda} = 0.67$             | $f_{\gamma\gamma} = 0.212$             |
| $f_{\sigma} = 1.955$                | $f_{\mu\mu} = -f_{\mu\mu}'' = 0.33$    |
| $f_{\pi\pi} = -f_{\pi\pi'} = 0.035$ | $f_{r\gamma} = -f_{r\gamma}'' = 0.225$ |
| $f_{\mu} = 3.216$                   |  |
| $f_{\mu\mu} = -0.277$               |  |

\* Stretching constants in mdyn/Å, deformation constants in mdyn Å/radian<sup>2</sup>, and stretch-bend interaction constants in mdyn/radian.

† Only the values of the stretching force constants can be uniquely determined from the symmetry force constants; for the computation of the remaining constants, the following assumptions were made:

$$f_{\mu\gamma} = f_{\mu\gamma}' = f_{\mu\gamma}'' = f_{\alpha\gamma} = f_{\alpha\beta} = 0, \quad f_{r\theta} = -f_{\theta r},$$

$$f_{\gamma} = -f_{\gamma''}, \quad \text{and} \quad \frac{f_{\theta}}{f_{\gamma}} = \frac{f_{\theta\theta}}{f_{\gamma\gamma}} = \frac{f_{\theta\theta'}}{f_{\gamma\gamma'}}$$

owing to the underdetermined nature of the force field. However, numerical experiments and comparisons with related molecules (see Table 5) indicate that the listed principal force constants might be expected to be a reasonable approximation of the general valence force field values.

Comparison of the  $\text{SF}_3\text{Br}$  stretching force constants with those of  $\text{SF}_6$  [14],  $\text{SF}_3\text{Cl}$  [5, 15],  $\text{SF}_5\text{O}$  [8] and  $\text{SeF}_3\text{Cl}$  [4] (see Table 5) shows the expected trends. The SF stretching force constant values decrease in the order:  $\text{SF}_6 > \text{SF}_3\text{Cl} > \text{SF}_3\text{Br} > \text{SF}_5\text{O}$ . This may be explained [4] by the decreasing electronegativity from F towards Br and the formal negative charge in  $\text{SF}_5\text{O}$  which all tend to release electron density to the remaining fluorine ligands. This results in an increased polarity ( $\text{S}^+ - \text{F}^-$ ) of these S—F bonds and, consequently, a lowering of the SF stretching force constants. The stretch-stretch interaction constants also show continuous trends, although it is difficult to rationalize why in

Table 5. Stretching force constants (in mdyn/Å) of SF<sub>5</sub>Br compared to those of SF<sub>5</sub>O, SF<sub>5</sub>Cl, SF<sub>6</sub>, SeF<sub>5</sub>Cl and SeF<sub>6</sub>.

|           | SF <sub>5</sub> Cl   |      |      | SF <sub>5</sub> Br | SF <sub>5</sub> O [8] | SeF <sub>6</sub> * | SeF <sub>5</sub> Cl [4] |
|-----------|----------------------|------|------|--------------------|-----------------------|--------------------|-------------------------|
|           | SF <sub>6</sub> [14] | [15] | [5]  |                    |                       |                    |                         |
| $f_R$     |                      | 4.83 | 4.62 | 4.50               | 3.75                  |                    | 4.42                    |
| $f_D$     | 5.26                 | 2.94 | 2.75 | 2.23               | 6.46                  | 5.01               | 2.75                    |
| $f_r$     |                      | 4.51 | 4.59 | 4.29               | 3.60                  |                    | 4.31                    |
| $f_{rr}$  | 0.341                | 0.30 | 0.26 | 0.27               | 0.54                  | 0.12               | 0.07                    |
| $f_{rr}'$ | 0.002                | 0.47 | 0.35 | 0.55               | 0.75                  | 0.14               | 0.35                    |
| $f_{RD}$  |                      | 0.44 | 0.4  | 0.67               | 0.66                  |                    |                         |

\* Abramowitz and I. W. Levin, *Inorg. Chem.*, **6**, 538 (1967).

$SF_0$  (for which a GVFF is known [14]) the value of  $f_n'$  becomes smaller than that of  $f_n$ . Generally, the interaction between linear bonds ( $f_n'$ ) is larger than that between bones at right angles ( $f_n$ ).

The potential energy distribution [16] for SF<sub>6</sub>Br is given in Table 6. As can be seen, most fundamentals are reasonably characteristic, thus supporting the above assignments. The mixing of the axial SF stretch ( $\nu_1$ ) with the equatorial SF<sub>6</sub> umbrella

**Table 6. Potential energy distribution for  $\text{SH}_5\text{Br}^*$**

|       |            |     |  |
|-------|------------|-----|--|
| $A_1$ | $\nu_1$    | 849 | $72F_{11} + 54F_{13} + 11F_{44} - 18F_{13} - 12F_{14}$ |
|       | $\nu_2$    | 692 | $100F_{22}$  |
|       | $\nu_3$    | 591 | $36F_{11} + 46F_{13} + 12F_{14}$                       |
|       | $\nu_4$    | 271 | $92F_{24}$   |
| $B_1$ | $\nu_5$    | 620 | $100F_{55}$  |
|       | $\nu_6$    | 470 | $100F_{66}$  |
| $B_2$ | $\nu_7$    | 500 | $100F_{77}$  |
| $E$   | $\nu_8$    | 894 | $85F_{88} + 14F_{99} + 19F_{10,10} - 14F_{89}$         |
|       | $\nu_9$    | 575 | $78F_{99} + 11F_{89}$                                  |
|       | $\nu_{10}$ | 418 | $14F_{88} + 71F_{10,10}$                               |
|       | $\nu_{11}$ | 222 | $93F_{11,11}$  |

\* Per cent contributions. Contributions of less than 10% to the PED are not listed.

Table 7. Computed thermodynamic properties of  $\text{SF}_5\text{Br}^+$ 

| T, K   | $C_p^\circ$ | $H^\circ - H^\circ_0$ | $-(F^\circ - H^\circ_0)/T$ | $S^\circ$ |
|--------|-------------|-----------------------|----------------------------|-----------|
| 0      | 0           | 0                     | 0                          | 0         |
| 100    | 9.916       | 0.844                 | 51.584                     | 60.020    |
| 200    | 15.763      | 2.121                 | 58.033                     | 68.637    |
| 298.15 | 20.527      | 3.918                 | 62.744                     | 75.883    |
| 300    | 20.598      | 3.956                 | 62.825                     | 76.010    |
| 400    | 23.619      | 6.179                 | 66.938                     | 82.386    |
| 500    | 25.459      | 8.640                 | 70.590                     | 87.870    |
| 600    | 26.619      | 11.248                | 73.875                     | 92.622    |
| 700    | 27.382      | 13.951                | 76.857                     | 96.787    |
| 800    | 27.909      | 16.717                | 79.583                     | 100.480   |
| 900    | 28.284      | 19.528                | 82.092                     | 103.790   |
| 1000   | 28.559      | 22.371                | 84.414                     | 106.785   |
| 1100   | 28.767      | 25.237                | 86.574                     | 109.517   |
| 1200   | 28.928      | 28.122                | 88.592                     | 112.027   |
| 1300   | 29.054      | 31.022                | 90.485                     | 114.348   |
| 1400   | 29.155      | 33.932                | 92.267                     | 116.505   |
| 1500   | 29.238      | 36.852                | 93.955                     | 118.519   |
| 1600   | 29.305      | 39.779                | 95.546                     | 120.408   |
| 1700   | 29.362      | 42.713                | 97.061                     | 122.187   |
| 1800   | 29.409      | 45.651                | 98.504                     | 123.866   |
| 1900   | 29.450      | 48.594                | 99.881                     | 125.457   |
| 2000   | 29.484      | 51.541                | 101.198                    | 126.969   |

\* Units for  $C_p^\circ$ ,  $S^\circ$ , and  $F^\circ$  are calories, moles, and degrees Kelvin; for  $H^\circ$  units are kilocalories and moles.

deformation ( $\nu_3$ ) is no surprise in view of their similar motions and frequencies.

#### Thermodynamic properties

The thermodynamic properties of SF<sub>6</sub>Br were computed with the molecular geometry and vibrational frequencies given above assuming an ideal gas at 1 atm pressure and using the harmonic-oscillator rigid-rotor approximation [17]. These properties are given for the range 0–2000 K in Table 7.

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Vibrational spectra of thionyl tetrafluoride, SF<sub>4</sub>O

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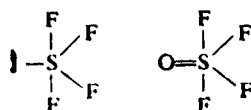
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**Abstract**—The i.r. spectra of gaseous, solid, and matrix-isolated SF<sub>4</sub>O and the Raman spectra of gaseous, liquid and solid SF<sub>4</sub>O are reported. It is shown that several bands previously attributed to SF<sub>4</sub>O belong to impurities, and 8 of the 12 fundamentals of SF<sub>4</sub>O were reassigned. A normal coordinate analysis was carried out and indicates for SF<sub>4</sub>O a structural model with significantly longer axial than equatorial S—F bonds, in disagreement with Gundersen and Hedberg's favored Model A. Thermodynamic properties are also reported for SF<sub>4</sub>O.

## INTRODUCTION

During a study of the vibrational spectra of SF<sub>4</sub> [1], we became also interested in those of SF<sub>4</sub>O. The molecular structures of these two molecules [2–6] are closely related and can both be derived from a trigonal bipyramid. The main difference between them is that in SF<sub>4</sub> one of the equatorial positions is occupied by a sterically active free valence electron pair, whereas in SF<sub>4</sub>O it is occupied by a doubly bonded oxygen atom.



A closer examination of the available literature data [7–9] on the vibrational spectra of SF<sub>4</sub>O revealed many discrepancies and indicated the need for a thorough reinvestigation. Our experimental data, which are reported in this paper, showed that several bands, previously attributed [7–9] to SF<sub>4</sub>O, actually belong to impurities, and resulted in the reassignment of 8 of the 12 fundamentals of SF<sub>4</sub>O.

## EXPERIMENTAL

Pure SF<sub>4</sub>O was prepared by vacuum pyrolysis of CsSF<sub>3</sub>O [10]. The complexing of crude SF<sub>4</sub>O with CsF [10] was found necessary in order to completely remove any SO<sub>2</sub>F<sub>2</sub> present. The latter does not form a stable adduct with CsF and can therefore be readily removed from CsSF<sub>3</sub>O by pumping.

Volatile compounds were manipulated in a well passivated (with ClF<sub>3</sub>) stainless steel vacuum line equipped with Teflon FEP U-traps and 316 stainless steel bellows-seal valves.

The i.r. spectra were recorded on a Perkin-Elmer Model 457 spectrophotometer in the range of 4000–250 cm<sup>-1</sup>. The instrument was calibrated by comparison with standard gas calibration points [11]. The gas cells were made of stainless steel with path lengths of either 5 or 10 cm. The windows were made of either AgCl, AgBr,

or high density polyethylene seasoned by ClF<sub>3</sub>. The apparatus, materials, and technique used for the matrix-isolation study have previously been described [12, 13].

The Raman spectra were recorded on a Cary Model 83 spectrophotometer using the 4880 Å exciting line. A Claassen filter was used to eliminate plasma lines [14]. Polarization measurements were carried out by method VIII as described by CLAASSEN *et al.* [14]. For the low-temperature spectra an apparatus was used similar to that described by MÜLLER and HARNEY [15]. A stainless steel cell with Teflon O-rings and sapphire windows [16] was used to obtain the spectrum of the gas. The sample containers for liquid and solid SF<sub>4</sub>O were either 3 mm o.d. quartz tubes or Teflon-FEP capillaries used in the transverse excitation-transverse viewing mode.

The <sup>19</sup>F NMR spectra were recorded at 56.4 MHz on a Varian Model DA-60 high resolution NMR spectrometer, equipped with a variable temperature probe. Chemical shifts were determined by the side-band technique relative to the external standard CFC1<sub>3</sub>. Teflon FEP tubes (Wilmad Glass Co.) were used as sample containers. Samples of neat SF<sub>4</sub>O, of SF<sub>4</sub>O over NaF (for removal of any HF possibly present), and of SF<sub>4</sub>O-FC1O<sub>2</sub> mixtures (1:3 mole ratio) over NaF showed only a single signal for SF<sub>4</sub>O over the entire liquid range (mp of FC1O<sub>2</sub>–147.75°C).

## RESULTS AND DISCUSSION

**Vibrational spectra.** Figure 1 shows the i.r. spectra of gaseous, solid and N<sub>2</sub>-matrix-isolated SF<sub>4</sub>O. Figure 2 shows the Raman spectra of gaseous, liquid, and solid SF<sub>4</sub>O. For the liquid phase, some variation in the spectra was observed. The spectra generally observed over a fairly wide temperature range are shown by traces D–F in Fig. 2. During one occasion, however, a spectrum was observed at –80°C which more closely resembled that of gaseous SF<sub>4</sub>O. It is shown as trace G in Fig. 2. Attempts to reproduce the spectrum with the same or other samples were unsuccessful, and the reason for its deviation could not be established. Figure 3 shows the most intense i.r. bands of gaseous and matrix-isolated SF<sub>4</sub>O at higher resolution

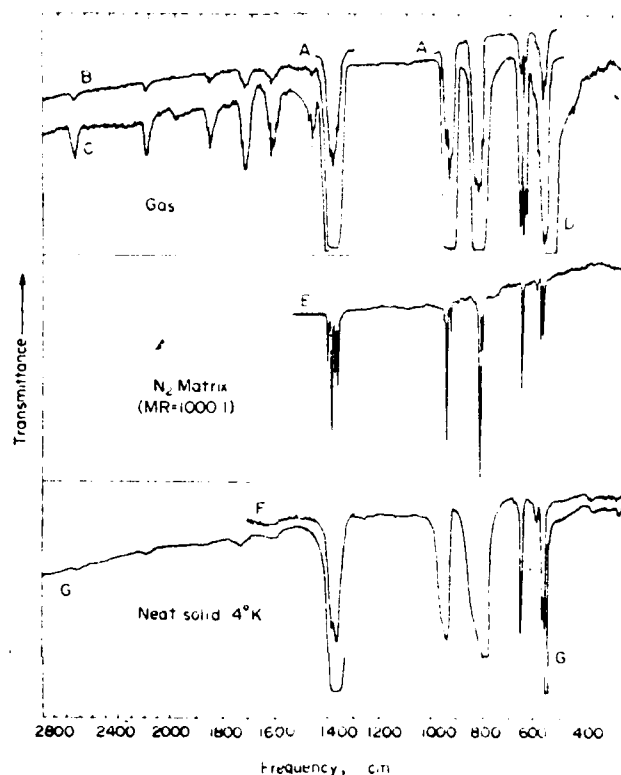


Fig. 1. Infrared spectra of  $\text{SF}_4\text{O}$ . Traces A-D, spectra of the gas at different pressures in a 5-cm path length cell. Trace A, 10 mm (AgBr windows); trace B, 75 mm (AgCl windows); trace C, 500 mm (AgBr windows); trace D, 1500 mm (polyethylene windows). Trace E, spectrum of  $\text{SF}_4\text{O}$  in a  $\text{N}_2$  matrix (mole ratio 1:1000) at 4 K. Traces F and G, spectra of neat solid  $\text{SF}_4\text{O}$  at two different sample thicknesses at 4 K (CsI windows).

and scale expansion, allowing some conclusions about the band contours and the determination of the  $^{32}\text{S}$ — $^{34}\text{S}$  isotopic shifts. The observed frequencies are listed in Table 1.

Comparison of the spectra of the gas, the liquid, and the solid shows only minor frequency shifts, indicating little association in the liquid and solid phase. This is in good agreement with its relatively low boiling point ( $-35.1^\circ\text{C}$ ) and Trouton constant (21.9) [7] and with the observations made for the similar molecule  $\text{ClF}_3\text{O}_2$  [17].

The trigonal-bipyramidal structure of  $\text{SF}_4\text{O}$  has been established by electron diffraction [3–5] and microwave [6] studies. However, four different models of symmetry  $C_{2v}$  were found [5] which were all in excellent agreement with the experimental electron diffraction data. No distinction between the four models was possible, but fortunately all of them are very similar as far as the vibrational assignments are concerned. Consequently, know-

ledge of the exact model is not necessary for making the assignments for  $\text{SF}_4\text{O}$ .

The 12 fundamentals expected for an  $\text{XY}_4\text{Z}$  molecule of symmetry  $C_{2v}$  can be classified as  $5A_1 + A_2 + 3B_1 + 3B_2$ . All of these should be active in both the i.r. and Raman spectra, except for the  $A_2$  mode which should be only Raman active.

**Assignment of the stretching modes.** The assignment of the stretching modes of  $\text{SF}_4\text{O}$  is relatively easy. There are three stretching modes in species  $A_1$ , i.e., the  $\text{S}=\text{O}$  stretch and the symmetric axial  $\text{SF}_2$  and the symmetric equatorial  $\text{SF}_2$  stretch. Of these, the  $\text{SO}$  double bond stretch,  $\nu_1$ , should have the highest frequency, should result in an intense i.r. and a polarized Raman band, and should occur above  $1000\text{ cm}^{-1}$ . Obviously, this fundamental must be assigned to the bands in the  $1350$ – $1390\text{ cm}^{-1}$  region. The splitting into four components in the matrix-isolation spectrum and the complex band contour in the i.r. spectrum of the gas are

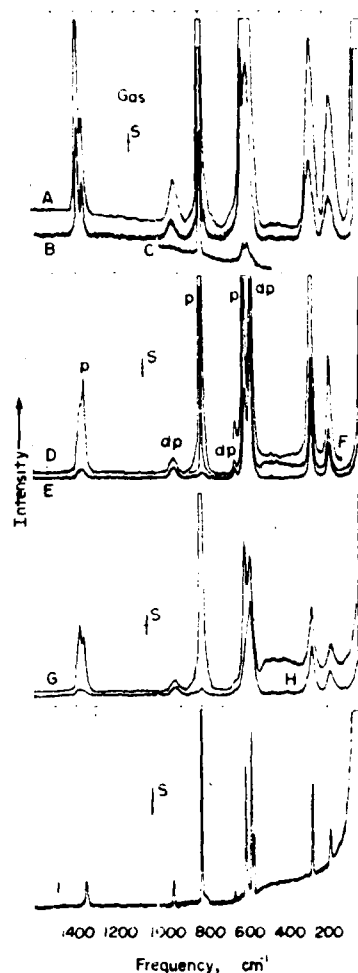


Fig. 2. Raman spectra of SF<sub>4</sub>O. Traces A-C, spectra of the gas at 10 atm pressure in a stainless steel cell with sapphire windows recorded at three different sensitivities. Traces D and E, characteristic spectrum of the liquid in a quartz capillary at -80° with the incident polarization perpendicular and parallel, respectively. The broad band between 300 and 500 cm<sup>-1</sup> is mainly due to quartz, as shown by trace F which was recorded for a sample contained in a Teflon-FEP capillary. Traces G and H, irreproducible spectrum of the liquid in a quartz capillary at -80° with the incident polarization perpendicular and parallel, respectively. Trace I, spectrum of solid SF<sub>4</sub>O in a quartz tube at -130°C.

caused by Fermi resonance between  $\nu_1$  and several  $A_1$  combination bands (see Table 1).

The symmetric equatorial SF<sub>2</sub> and axial SF<sub>2</sub> stretching modes  $\nu_2$  and  $\nu_3$  should give rise to two strong polarized Raman bands in the frequency

range 500–1000 cm<sup>-1</sup>. Since the equatorial SF<sub>2</sub> group is strongly bent, its symmetric stretching mode should result in an intense i.r. band, whereas for the almost linear axial SF<sub>2</sub> group the symmetric stretch should be of low i.r. intensity. Furthermore, by comparison with similar pseudo-trigonal bipyramidal molecules [1, 17], the symmetric equatorial stretch should have a significantly higher frequency than the axial one. Accordingly, the symmetric equatorial SF<sub>2</sub> and the symmetric axial SF<sub>2</sub> stretching modes are readily assigned to the bands at about 796 and 588 cm<sup>-1</sup>, respectively. For the observation of  $\nu_2$  and  $\nu_3$  in the i.r. spectra, the matrix isolation data (see Fig. 3) were helpful since  $\nu_2$  almost coincides with  $\nu_7$  (B<sub>1</sub>), and  $\nu_3$  occurs in the vicinity of two i.r. bands of higher intensity.

There are two antisymmetric SF<sub>2</sub> stretching modes, the equatorial one,  $\nu_{10}$  (B<sub>2</sub>), and the axial one,  $\nu_7$  (B<sub>1</sub>). Both should occur in the frequency range 700–1000 cm<sup>-1</sup> and be very intense in the i.r. spectrum. In the Raman spectra,  $\nu_{10}$  should be considerably more intense than  $\nu_7$  because of the large difference in the equatorial and axial SF<sub>2</sub> bond angles. Consequently,  $\nu_{10}$  (B<sub>2</sub>) and  $\nu_7$  (B<sub>1</sub>) can be assigned with confidence to the bands at about 926 and 819 cm<sup>-1</sup>, respectively. The i.r. band contour of  $\nu_7$  (see Fig. 3) is complicated by  $\nu_2$  (A<sub>1</sub>) which has a similar frequency (see above) and by Fermi resonance with  $\nu_5 + \nu_8$  (B<sub>1</sub>).

**Assignment of the deformation modes.** The assignment of the remaining bands to the seven deformation modes is more difficult, since only five intense bands (at about 639, 567, 560, 265 and 174 cm<sup>-1</sup>) were observed with the possibility of a sixth weak fundamental at about 455 cm<sup>-1</sup>. A similar situation was encountered for SF<sub>4</sub> [1]. It is very difficult to decide if the lack of observation of a fundamental is caused either by its low intensity or by a coincidence of two fundamentals. Tentative assignments for the SF<sub>4</sub>O deformation modes can be made based on the following arguments.

The 639 cm<sup>-1</sup> band has too high a frequency for an SF<sub>2</sub> deformation and, therefore, should be due to the S=O wagging mode,  $\nu_6$  (B<sub>1</sub>). Additional support for this assignment comes from the i.r. gas phase band contour which is similar to  $\nu_7$  (B<sub>1</sub>) (see Fig. 3). Furthermore, there is some evidence in the i.r. spectrum of the gas for Fermi resonance between  $\nu_7$  (B<sub>1</sub>) and the 174 + 639 cm<sup>-1</sup> combination band. Since the 174 cm<sup>-1</sup> band belongs to species A<sub>1</sub> (see below), the 639 cm<sup>-1</sup> mode must belong to species B<sub>1</sub>.

The lowest frequency mode (174 cm<sup>-1</sup>) should be the one involved in an intramolecular Berry-type

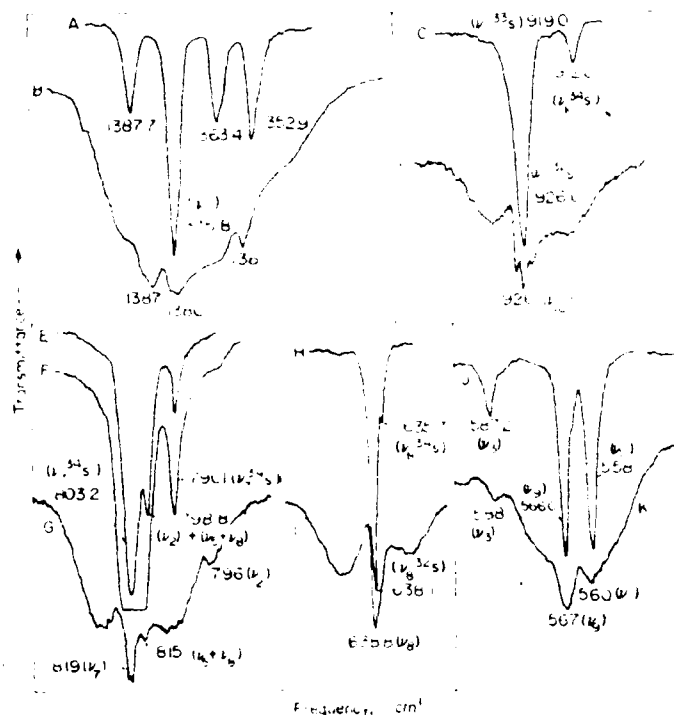


Fig. 3. Principal i.r. bands of gaseous and  $N_2$ -matrix-isolated  $SF_4O$  recorded at tenfold scale expansion under higher resolution conditions. The frequency scale of the gas and matrix spectra have been slightly shifted relative to each other to allow better comparison.

exchange mechanism [1]. Consequently, the  $174\text{ cm}^{-1}$  Raman band is assigned to  $\nu_3(A_1)$  by analogy with  $SF_4$  [1]. The relative ease of intramolecular exchange in  $SF_4O$  was confirmed by our failure to observe separate  $^{19}F$ NMR signals for the equatorial and axial fluorines in  $SF_4O$  at temperatures as low as  $-145^\circ\text{C}$ . Polarization measurements on the liquid provided no direct evidence for the  $174\text{ cm}^{-1}$  fundamental being polarized. Similarly, all the other deformation modes also had a depolarization ratio of 0.75. However, a polarized combination band ( $588 + 174$ ) in Fermi resonance with  $\nu_2(A_1)$  was observed. Since the  $588\text{ cm}^{-1}$  band has been established (see above) as an  $A_1$  mode, the  $174\text{ cm}^{-1}$  band must also belong to species  $A_1$ .

By comparison with the closely related  $PF_3$  [18] and  $SF_4$  [1] molecules, the equatorial  $SF_2$  wagging deformation  $\nu_6(B_2)$  of  $SF_4O$  should be of high Raman and of medium i.r. intensity and have a frequency between  $500$  and  $600\text{ cm}^{-1}$ . It is therefore assigned to the higher frequency component of the two bands observed in the  $550$ – $570\text{ cm}^{-1}$  region.

Ignoring for the time being the  $A_2$  torsional mode, we still need assignments for the antisymmetric equatorial  $OSF_2$  in plane deformation  $\nu_{11}(B_2)$ , the equatorial  $SF_2$  scissoring mode  $\nu_4(A_1)$ , and the axial  $SF_2$  out of plane scissoring mode  $\nu_{12}(B_2)$ . The following bands are still unassigned: (i) a band at about  $560\text{ cm}^{-1}$  of medium intensity in both the i.r. and Raman spectrum; (ii) a band at about  $270\text{ cm}^{-1}$  of medium strong Raman and of low i.r. intensity; (iii) a band at about  $450\text{ cm}^{-1}$  of low intensity in both the i.r. and Raman spectrum. By comparison with the known spectrum of planar  $OCF_2$  [19],  $\nu_{11}$  of  $SF_4O$  is expected to have a higher frequency and Raman intensity than  $\nu_4$ . Furthermore, the frequency of  $\nu_{12}(B_2)$  should be lower than those of  $\nu_{11}$  and  $\nu_4$  and by comparison with other similar molecules [1, 17, 18, 20] might be expected to be either degenerate with or close to that of the in plane axial  $SF_2$  scissoring mode  $\nu_3$  ( $174\text{ cm}^{-1}$ ). Consequently, the  $560\text{ cm}^{-1}$  band of  $SF_4O$  should be due to  $\nu_{11}(B_2)$ .

For the assignment of the  $270\text{ cm}^{-1}$  band of  $SF_4O$ , two alternatives remain,  $\nu_4(A_1)$  and  $\nu_{12}(B_2)$ .

We prefer its assignment to  $\nu_{12}$  ( $B_2$ ) for the following reasons: (i) its relatively low frequency value is more in line with our expectations for  $\nu_{12}$  (see above); (ii) its relative i.r. and Raman intensities do not correspond well to those observed for the CF<sub>2</sub> scissoring in planar OCF<sub>2</sub> [19]; (iii) for ClF<sub>3</sub>O<sub>2</sub> two intense low-frequency Raman bands were observed [17] at 222 and 285 cm<sup>-1</sup>, respectively, which resemble those at 185 and 268 cm<sup>-1</sup> observed for SF<sub>4</sub>O. Therefore, these two Raman bands should belong to a structural element common to both ClF<sub>3</sub>O<sub>2</sub> and SF<sub>4</sub>O. Since ClF<sub>3</sub>O<sub>2</sub> contains only one equatorial F atom [17, 21], this common structural element must be the axial F-XF group, and the two modes should be due to the axial in plane and out of plane scissoring modes. The assignments previously made [17] for these two modes in ClF<sub>3</sub>O<sub>2</sub> should be reversed.

All the observed bands are now assigned, except for a very weak i.r. and Raman band at about 450 cm<sup>-1</sup>. This band could either be due to the still unassigned  $\nu_4$  ( $A_1$ ) fundamental or the 174 + 265 = 439 cm<sup>-1</sup> combination band. Its assignment to the  $\nu_3$  ( $A_2$ ) torsional mode is unlikely based on its activity in the i.r. spectrum of gaseous SF<sub>4</sub>O. Since the observed frequency (~450 cm<sup>-1</sup>) does not agree too well with that of 439 cm<sup>-1</sup>, calculated for  $\nu_3 + \nu_{12}$ , we tentatively assign the 450 cm<sup>-1</sup> band to  $\nu_4$  ( $A_1$ ). However, the relatively low i.r. intensity of the 450 cm<sup>-1</sup> band is disturbing for this assignment, and the possibility cannot be ruled out that  $\nu_4$  ( $A_1$ ) might occur in the 560 cm<sup>-1</sup> region, but is difficult to detect owing to the presence of three other nearby fundamentals.

Except for the  $A_2$  torsional mode, all fundamentals of SF<sub>4</sub>O have thus been assigned. The assignments for all stretching modes and most of the deformations can be considered firm. The  $A_2$  torsional mode which should be only Raman active could not be positively identified. It is expected to occur in the region 400–550 cm<sup>-1</sup> in which several extremely weak and therefore questionable Raman features were observed.

**Combination bands.** A further point in support of the above assignments are the combination bands. All observed combination bands could be assigned (see Table 1) without violation of the selection rules for  $C_{2v}$  ( $B_1 + B_2 = A_2$  and  $A_1 + A_2 = A_2$  combinations are i.r. forbidden). Furthermore, for cases involving Fermi resonance, the corresponding fundamentals and combination bands belonged always to the same symmetry species.

**Band contours.** The i.r. gas phase band contours were also examined. Based on the published mic-

rowave data ( $A = 0.13663$ ,  $B = 0.11204$ ,  $C = 0.10808$  cm<sup>-1</sup>) [6], the band contours of SF<sub>4</sub>O should approximate those of set 39 in the tables of UEDA and SHIMANOUCHI [22]. Since the  $B$  and  $C$  values are quite similar, the  $B$  and  $C$  type bands should be similar under our resolution conditions, and the  $A$  type bands should show a narrower  $Q$  branch. Since the  $A$  axis (smallest moment of inertia) obviously must lie in the direction of the F<sub>ax</sub>—S—F<sub>ax</sub> bonds, the  $B_1$  modes should exhibit a narrower  $Q$  branch. The observed band contours of  $\nu_7$  and  $\nu_8$  (see Fig. 3) agree well with this prediction. The largest moment of inertia should be along the S=O axis. Therefore, the  $A_1$  modes should exhibit  $C$  type band contours, and the  $B_2$  modes should show a  $B$  type contour with a double  $Q$  branch. Based on these arguments, we prefer to attribute the complex structure observed for the  $Q$  branch of the 926 cm<sup>-1</sup>  $\nu_{10}$  ( $B_2$ ) band to hot bands. Unfortunately, most of the band contours observed for SF<sub>4</sub>O are complicated by effects, such as coincidence of several fundamentals, Fermi resonance, <sup>32</sup>S—<sup>34</sup>S isotopic splittings, and possibly hot bands. The only band having a relatively undisturbed contour is  $\nu_8$  ( $B_1$ ) at 639 cm<sup>-1</sup>.

**Isotopic splittings.** The natural abundances of the sulfur isotopes are: <sup>32</sup>S = 95.06, <sup>33</sup>S = 0.74 and <sup>34</sup>S = 4.18%. For some of the fundamentals splittings due to these isotopes were observed in the matrix isolation i.r. spectra and are listed in Table 1 and Fig. 3.

**Comparison with related molecules.** A comparison of the assignments for SF<sub>4</sub>O to those previously made for the related molecules SF<sub>4</sub> [1], ClF<sub>3</sub> [20], and ClF<sub>3</sub>O<sub>2</sub> [17] is given in Table 2. For ClF<sub>3</sub> and ClF<sub>3</sub>O<sub>2</sub> only the modes associated with the F<sub>ax</sub>—Cl—F<sub>ax</sub> group are listed to avoid confusion. The general agreement is relatively good, if the following points are kept in mind: (i) In the chlorine fluorides, the central atom is more electronegative than oxygen. Consequently, oxygen addition results in an electron release to chlorine and weakens the Cl—F bonds by increasing their polarity. For sulfur fluorides, the effect is reverse because oxygen is more electronegative than the sulfur atom. (ii) In SF<sub>4</sub>O, coupling between  $\nu_1$  and  $\nu_2$  increases their frequency difference and results in a frequency value for  $\nu_2$  which is surprisingly low by comparison with that found for SF<sub>4</sub>.

As can be seen from Table 2, the problems associated with the assignment of the deformation modes in these pseudo-trigonal bipyramidal molecules are not trivial and more information is required before these assignments should be

Table 1. Vibrational spectra of SF<sub>6</sub>O and their assignment in point group C<sub>2v</sub>

| Gas      | Matrix Isolated | Solid | Neat    | Obsd freq, cm <sup>-1</sup> , and intensity* |              |       | Assignment†  |
|----------|-----------------|-------|---------|--|--------------|-------|--|
|          |                 |       |         | Gas‡   | Raman Liquid | Solid |  |
| 2740 vw  |                 |       | 2720 vw |  |              |       | 2ν <sub>1</sub> (A <sub>1</sub> )  |
| 2188 vw  |                 |       | 2180 vw |  |              |       | ν <sub>1</sub> + ν <sub>2</sub> (B <sub>1</sub> )                                      |
| 1852 vw  |                 |       |         |  |              |       | ν <sub>1</sub> + ν <sub>2</sub> (A <sub>1</sub> )                                      |
| 1716 vw  |                 |       | 1725 vw |  |              |       | 2ν <sub>10</sub> (A <sub>1</sub> )   |
| 1619 vw  |                 |       | 1600 vw |  |              |       | ν <sub>2</sub> + ν <sub>10</sub> (B <sub>2</sub> )                                     |
| 1600 vw  |                 |       |         |  |              |       | ν <sub>2</sub> + ν <sub>10</sub> (A <sub>1</sub> )                                     |
| 1459 vw  |                 |       |         |  |              |       | 2ν <sub>2</sub> (A <sub>1</sub> )  |
| 1387     | 1387.7 m        |       |         |  |              |       | ν <sub>7</sub> + ν <sub>8</sub> (A <sub>1</sub> )                                      |
| 1380     | 1375.8 s        |       |         |  |              |       | ν <sub>7</sub> + ν <sub>8</sub> (A <sub>1</sub> )                                      |
| 1361     | 1363.4 m        |       |         |  |              |       | ν <sub>1</sub> (A <sub>1</sub> )   |
|          | 1352.9 ms       |       |         |  |              |       | ν <sub>2</sub> + ν <sub>3</sub> (A <sub>1</sub> )                                      |
|          | 1339.7 w        |       |         |  |              |       | ν <sub>2</sub> + ν <sub>3</sub> (A <sub>1</sub> )                                      |
| 926 s    | 926.0 s         |       |         |  |              |       | ν <sub>4</sub> + ν <sub>5</sub> + ν <sub>6</sub> (A <sub>1</sub> )                     |
|          | 919.0 w         |       |         |  |              |       | ν <sub>4</sub> + ν <sub>5</sub> + ν <sub>6</sub> (A <sub>1</sub> )                     |
|          | 912.0 mw        |       |         |  |              |       | 2ν <sub>3</sub> + ν <sub>4</sub> (A <sub>1</sub> )                                     |
| 819 vs   | 803.2 vs        |       |         |  |              |       | ν <sub>10</sub> ( <sup>32</sup> Si)(B <sub>2</sub> )                                   |
| 815 m    | 798.8 m         |       |         |  |              |       | ν <sub>10</sub> ( <sup>34</sup> Si)(B <sub>2</sub> )                                   |
|          | 790.1 m         |       |         |  |              |       | ν <sub>7</sub> ( <sup>32</sup> Si)(B <sub>1</sub> )                                    |
| 796 m    | 798.8 mw        |       |         |  |              |       | ν <sub>7</sub> + ν <sub>8</sub> (B <sub>1</sub> )                                      |
|          |                 |       |         |  |              |       | ν <sub>7</sub> ( <sup>34</sup> Si)(B <sub>1</sub> )                                    |
|          |                 |       |         |  |              |       | ν <sub>2</sub> (A <sub>1</sub> )   |
| 636.8 ms | 638.1 ms        |       |         |  |              |       | ν <sub>3</sub> + ν <sub>4</sub> (A <sub>1</sub> )                                      |
|          | 635.7 w         |       |         |  |              |       | ν <sub>8</sub> ( <sup>32</sup> Si)(B <sub>2</sub> )                                    |
| 588 mw   | 587.2 mw        |       |         |  |              |       | ν <sub>8</sub> ( <sup>34</sup> Si)(B <sub>2</sub> )                                    |
| 567 ms   | 566.0 ms        |       |         |  |              |       | ν <sub>3</sub> (A <sub>1</sub> )   |
| 560 ms   | 558.1 ms        |       |         |  |              |       | ν <sub>6</sub> (B <sub>2</sub> )   |
| 447 vvw  |                 |       |         |  |              |       | ν <sub>11</sub> (B <sub>2</sub> )  |
| 270 vw   |                 |       |         |  |              |       | ν <sub>5</sub> + ν <sub>12</sub> (B <sub>2</sub> ) or ν <sub>4</sub> (A <sub>1</sub> ) |
|          |                 |       |         |  |              |       | ν <sub>12</sub> (B <sub>2</sub> )  |
|          |                 |       |         |  |              |       | ν <sub>4</sub> (A <sub>1</sub> )   |

\* Uncorrected Raman intensities representing the relative peak height; the relative peak widths and, hence, the relative peak heights change for the different phases.

† The assignments for some of the deformation modes are tentative.

‡ Only qualitative polarization measurements could be obtained for the gas, owing to the optical activity of the sapphire windows of the gas cell.

§ Spectrum of trace G of Fig. 2.

\*\* Spectrum of traces D-F of Fig. 2.

Vibrational spectra of thionyl tetrafluoride, SF<sub>4</sub>O

Table 2. Vibrational spectra of SF<sub>4</sub>O compared to those of SF<sub>4</sub>, ClF<sub>3</sub> and ClF<sub>3</sub>O<sub>2</sub>

| ClF <sub>3</sub> [20] |          | ClF <sub>3</sub> O <sub>2</sub> [17] |          | SF <sub>4</sub> [1] |            | SF <sub>4</sub> O |             | Assignment<br>for SF <sub>4</sub> O in<br>point group<br>C <sub>2v</sub> | Approx. description<br>of mode for SF <sub>4</sub> O          |
|-----------------------|----------|--------------------------------------|----------|---------------------|------------|-------------------|-------------|--|---|
| i.r.                  | Ra       | i.r.                                 | Ra       | i.r.                | Ra         | i.r.              | Ra          |  |   |
| 530 m                 | 529 vs.p | 487 vw                               | 487(6) p | 892 s               | 893(9.2) p | 1380 vs           | 1380(0.7) p | A <sub>1</sub> ν <sub>1</sub>  | S=O stretch   |
|                       |          |                                      |          | 558 m               | 558(10) p  | 796 m             | 795(10) p   | ν <sub>2</sub>   | sym equat SF <sub>2</sub> stretch                             |
|                       |          |                                      |          | 353                 | 356(0+)    | 588 mw            | 587(1.7) p  | ν <sub>3</sub>   | sym axial SF <sub>2</sub> stretch                             |
| 328                   | 329 w, p |                                      | 222(1)   | 226 w               | 229(1.0)   | 447 vw            | 455(0+)     | ν <sub>4</sub>   | equat SF <sub>2</sub> scissor                                 |
|                       |          |                                      |          |                     | 474(0.7)   |                   | 174(0.4)    | ν <sub>5</sub>   | axial SF <sub>2</sub> scissor in F <sub>ax</sub> SO plane     |
| 702 vs                |          | 695 vs                               |          | 728 vs              | 730(0.5)   | 819 vs            | 815 sh      | A <sub>2</sub> ν <sub>6</sub>  | torsion   |
|                       |          |                                      |          |                     |            | 639 ms            | 640 sh      | B <sub>1</sub> ν <sub>7</sub>  | antisym axial SF <sub>2</sub> stretch                         |
|                       |          |                                      |          | 532 ms              | 535(3.5)   | 567 ms            | 566(1.7)    | ν <sub>8</sub>   | S=O wagging   |
|                       |          |                                      |          | 867 s               | 865 sh     | 926 s             | 924(0.2)    | B <sub>2</sub> ν <sub>10</sub>   | equat SF <sub>2</sub> wagging                                 |
|                       |          |                                      |          | 353 ms              | 356(0+)    | 560 ms            | 566         | ν <sub>11</sub>  | antisym equat SF <sub>2</sub> stretch                         |
| 328 s                 | 329 w    | 287 w                                | 285(1)   |                     |            | 1270 vw           | 265(0.7)    | ν <sub>12</sub>  | equat SF <sub>2</sub> rocking                                 |
|                       |          |                                      |          |                     |            |                   |             |  | axial SF <sub>2</sub> scissor out of F <sub>ax</sub> SO plane |

considered as being well established. A large number of suitable molecules, such as SF<sub>4</sub>, SF<sub>4</sub>O, ClF<sub>3</sub>, ClF<sub>3</sub>O, ClF<sub>3</sub>O<sub>2</sub>, PF<sub>3</sub>, PF<sub>3</sub>X and PF<sub>3</sub>X<sub>2</sub>, are available and are ideally suited for a systematic study. Unfortunately, such a systematic study is beyond the scope of the present investigation.

**Force constants.** A normal coordinate analysis was carried out for SF<sub>4</sub>O to support the above assignments. The potential and kinetic energy metrics were computed by a machine method [23]. The geometry used for the computation was model D of GUNDENSEN and HEDBERG [5] since it agrees best with the microwave data [6]. The symmetry coordinates used were analogous to those previously given for ClF<sub>3</sub>O<sub>2</sub> [17], except for exchanging the equatorial oxygen atoms for fluorines and vice versa (see Fig. 4). As in that work, the redundant coordinate in the A<sub>1</sub> block was found from the numerical B matrix, and the deformation coordinates were made orthogonal to the redundancy by the Gram-Schmidt process. The bending coordinates were weighted by unit (1 Å) distance. The G matrix and Z transformation were found numerically by the computer and, hence, only the coefficients for the more important force constants are given in Table 3.

The force constants were adjusted by trial and error with the aid of a computer to give an exact fit between the observed and computed frequencies. The observed <sup>32</sup>S—<sup>34</sup>S isotopic shifts were used as additional constraints (see Table 3). For example, for the A<sub>1</sub> block a diagonal valence force field (DVFF) results in an isotopic shift of 17.4 cm<sup>-1</sup> for ν<sub>1</sub> and an unreasonably (see below) low value of 11.05 mdyn/Å for the SO stretching force constant. Based on intensity arguments, ν<sub>1</sub> (<sup>34</sup>S) is best as-

cribed to the shoulder on the 1363.4 cm<sup>-1</sup> band (see trace A of Fig. 3) indicating an isotopic shift of 15 cm<sup>-1</sup> for ν<sub>1</sub>. With this constraint, a force field (MVFF I) is obtained which results in a more plausible value for F<sub>11</sub> (see below) and a more characteristic potential energy distribution (see Table 3).

For the B<sub>1</sub> block two solutions were found (see Table 3) which were capable of duplicating the observed isotopic shifts. Their main difference is the sign of f<sub>RR</sub>. Since a value of 0.28 mdyn/Å for f<sub>RR</sub> agrees much better with the values found for related molecules (see Table 4), we prefer set I of Table 3 over set II, although the PED of set II is more characteristic. Strong mixing of the modes in B<sub>1</sub> would not be surprising in view of their similar frequencies and their ease of coupling. An exact duplication of the observed matrix isolation isotopic shifts could be achieved by using for ν<sub>7</sub> the observed matrix isolation frequency value (803 cm<sup>-1</sup>) in place of the gas phase value (819 cm<sup>-1</sup>). The resulting force field was almost identical to MVFF I (see Table 3) and, therefore, is not separately listed. Contrary to the findings for the B<sub>1</sub> block, the potential energy distribution for the A<sub>1</sub> and B<sub>2</sub> blocks is highly characteristic.

A comparison of the stretching force constants of SF<sub>4</sub>O with those previously reported for similar molecules [24–35] is given in Table 4 and shows the expected trends. The equatorial SF bonds in SF<sub>4</sub>O are significantly stronger than the axial ones (even if MVFF II is chosen), thus supporting our choice of an electron diffraction data model [5] in which rSF<sub>eq</sub> is significantly shorter than rSF<sub>ax</sub>. By analogy with the other related pseudotrigonal-bipyramidal sulfur or chlorine fluorides or oxyfluorides, the bonding in SF<sub>4</sub>O might be described

Table 3. Observed frequencies ( $\text{cm}^{-1}$ ), symmetry force constants\*, computed and observed  $^{32}\text{S}$ - $^{34}\text{S}$  isotopic shifts ( $\text{cm}^{-1}$ ), and potential energy distribution† for  $\text{SF}_6\text{O}$ 

|                    | Frequency  | F  | $\Delta\nu_{\text{COMP}}$ | $\Delta\nu_{\text{OBSD}}$ | MVFF I |   | F      | $\Delta\nu_{\text{COMP}}$ | DVFF   |                           | PED  |
|--------------------|------------|--|---------------------------|---------------------------|--------|---|--------|---------------------------|--------|---------------------------|--|
|                    |            |  |                           |                           | PED    | PED   |        |                           | F      | $\Delta\nu_{\text{COMP}}$ |  |
| $A_1$              | $\nu_1$    | $F_{11} = f_0$   | 11.990                    | 14.8                      | -15    | 100F <sub>11</sub>  | 11.05  | 17.4                      | 11.05  | 17.4                      | 89F <sub>11</sub>  |
|                    | $\nu_2$    | $F_{22} = f_1 + f_{11}$  | 5.951                     | 2.4                       |        | 100F <sub>22</sub>  | 5.98   | 1.8                       | 5.98   | 1.8                       | 88F <sub>22</sub> + 10F <sub>11</sub>  |
|                    | $\nu_3$    | $F_{33} = f_2 + f_{22}$  | 3.825                     | 0.1                       |        | 98F <sub>33</sub>   | 3.83   | 0.1                       | 3.83   | 0.1                       | 99F <sub>33</sub>  |
|                    | $\nu_4$    | $F_{44} = 0.32(2f_3 + f_0) + 0.15(2f_1 + f_2)$                     | 1.440                     | 1.6                       |        | 100F <sub>44</sub>  | 1.45   | 1.0                       | 1.45   | 1.0                       | 94F <sub>44</sub>  |
|                    | $\nu_5$    | $F_{55} = 0.24(2f_4 + f_0) + 0.16(f_1 + f_2) + 0.27(2f_3 + f_2)$   | 0.1486                    | 0.7                       |        | 96F <sub>55</sub>   | 0.1475 | 0.8                       | 0.1475 | 0.8                       | 97F <sub>55</sub>  |
| $A_2$              | $\nu_6$    | $F_{12} = \sqrt{2}f_{12}$  | 1.1                       |                           |        |   |        |                           |        |                           |  |
|                    | $\nu_7$    | $F_{24} = 0.56(2f_{12} - f_{11} - f_{22}) + 0.24(f_{11} - f_{22})$ | -0.7                      |                           |        |   |        |                           |        |                           |  |
|                    | $\nu_8$    | $F_{34} = f_3 - f_{12} - f_{22} + f_{33}$                          | 1.279                     | 0                         |        | 100F <sub>44</sub>  |        |                           |        |                           |  |
| $B_1$              | $\nu_9$    | $F_{11} = f_0$   | 1.803                     |                           |        |   |        |                           |        |                           |  |
|                    | $\nu_{10}$ | $F_{22} = f_1 - f_{11}$  | 2.417                     |                           |        |   |        |                           |        |                           |  |
|                    | $\nu_{11}$ | $F_{33} = f_2 - f_{22}$  | 3.26                      | 13.4                      | 13.1   | 63F <sub>77</sub> + 64F <sub>88</sub> + 10F <sub>99</sub> - 13F <sub>10</sub> - 17F <sub>11</sub> | 4.303  | 13.0                      | 4.303  | 13.0                      | 124F <sub>77</sub> + 10F <sub>88</sub> + 18F <sub>99</sub> - 23F <sub>10</sub> - 28F <sub>11</sub> |
| $B_2$              | $\nu_{12}$ | $F_{12} = f_1 - f_{11}$  | 2.77                      | 2.4                       | 2.4    | 41F <sub>77</sub> + 25F <sub>88</sub> + 48F <sub>99</sub> - 31F <sub>10</sub>                     | 2.359  | 1.8                       | 2.359  | 1.8                       | 104F <sub>88</sub>   |
|                    | $\nu_{13}$ | $F_{23} = f_2 - f_{22} + f_{33} - f_{34}$                          | 2.63                      | 1.0                       | 1-2    | 12F <sub>77</sub> + 15F <sub>88</sub> + 60F <sub>99</sub> + 18F <sub>10</sub>                     | 2.470  | 1.9                       | 2.470  | 1.9                       | 94F <sub>99</sub>  |
|                    | $\nu_{14}$ | $F_{34} = f_3 - f_{12} - f_{22} + f_{33}$                          | 0.31                      |                           |        |   | 1.02   |                           | 1.02   |                           |  |
|                    | $\nu_{15}$ | $F_{45} = \sqrt{2}(f_{12} - f_{34})$                               | 1.01                      |                           |        |   | 0.95   |                           | 0.95   |                           |  |
|                    | $\nu_{16}$ | $F_{56} = \sqrt{2}(f_{12} - f_{34})$                               | -0.37                     |                           |        |   | -0.15  |                           | -0.15  |                           |  |
| MATRIX FREQUENCIES | $\nu_{17}$ | $F_{10,10} = f_1 - f_{11}$   | 5.415                     | 14.0                      | 14.0   | 103F <sub>10,10</sub> + 11F <sub>11,11</sub> - 18F <sub>10,11</sub>                               |        |                           |        |                           |  |
|                    | $\nu_{18}$ | $F_{11,11} = f_1 - f_{11}$   | 1.459                     | 2.7                       |        | 91F <sub>11,11</sub>  |        |                           |        |                           |  |
|                    | $\nu_{19}$ | $F_{12,12} = f_2 - f_{22}$   | 1.023                     | 0.6                       |        | 94F <sub>12,12</sub>  |        |                           |        |                           |  |
|                    | $\nu_{20}$ | $F_{13,13} = f_3 - f_{33}$   | 0.75                      |                           |        |   |        |                           |        |                           |  |
|                    | $\nu_{21}$ | $F_{14,14} = f_4 - f_{44}$   | 3.24                      | 13.1                      | 13.1   | 66F <sub>77</sub> + 64F <sub>88</sub> + 10F <sub>99</sub> - 15F <sub>10</sub> - 18F <sub>11</sub> |        |                           |        |                           |  |
| $B_2$              | $\nu_{22}$ | $F_{23} = f_2 - f_{22} + f_{33} - f_{34}$                          | 2.70                      | 2.4                       | 2.4    | 41F <sub>77</sub> + 26F <sub>88</sub> + 47F <sub>99</sub> - 31F <sub>10</sub> + 9F <sub>11</sub>  |        |                           |        |                           |  |
|                    | $\nu_{23}$ | $F_{34} = f_3 - f_{12} - f_{22} + f_{33}$                          | 2.62                      | 1.1                       | 1-2    | 11F <sub>77</sub> + 15F <sub>88</sub> + 62F <sub>99</sub> + 18F <sub>10</sub>                     |        |                           |        |                           |  |
|                    | $\nu_{24}$ | $F_{45} = \sqrt{2}(f_{12} - f_{34})$                               | 0.35                      |                           |        |   |        |                           |        |                           |  |
|                    | $\nu_{25}$ | $F_{56} = \sqrt{2}(f_{12} - f_{34})$                               | 1.02                      |                           |        |   |        |                           |        |                           |  |
|                    | $\nu_{26}$ | $F_{67} = f_6 - f_{66}$  | -0.36                     |                           |        |   |        |                           |        |                           |  |

\* Stretching constants in  $\text{mdyn}/\text{\AA}$ , deformation constants in  $\text{mdyn}/\text{\AA}^2$ , and stretch-bend interaction constants in  $\text{mdyn}/\text{radian}$ .

† Percent contributions. Contributions of less than 9% to the PED are not listed.



Table 4. Stretching force constants (mdyn Å) of SF<sub>4</sub>O compared to those of similar molecules

|             | SF <sub>6</sub> [24] | SF <sub>4</sub> O | SF <sub>2</sub> O <sub>2</sub> [25] | SO <sub>2</sub> [26] | SF <sub>6</sub> [1] | SF <sub>2</sub> O[27] | SO <sub>2</sub> [28] | SF <sub>2</sub> [29] | SO[30] | ClF <sub>3</sub> O <sub>2</sub> [17] | FCIO <sub>3</sub> [31] | ClF <sub>3</sub> O[32] | FCIO <sub>2</sub> [33] | ClF <sub>3</sub> [34] | FCIO[35] |
|-------------|----------------------|-------------------|-------------------------------------|----------------------|---------------------|-----------------------|----------------------|----------------------|--------|--------------------------------------|------------------------|------------------------|------------------------|-----------------------|----------|
| $f_{r=0}$   | 11.99                | 11.63             | 10.61                               | 11.22                | 10.42               | 8.12                  | 9.23                 | 9.4                  | 9.37   | 9.07                                 | 6.85                   | 4.19                   | 2.70                   | 0.35                  | 0.35     |
| $f_{r(eq)}$ | 5.26                 | 5.68              | 5.51                                | 4.07                 | 4.78                | 0.39                  | 3.35                 | 3.9                  | 3.16   | 2.53                                 | 2.59                   | 2.70                   | 0.35                   | 0.35                  | 0.35     |
| $f_{r(ax)}$ | 3.54                 | 3.30              | 0.25                                | 0.35                 | 0.39                | 0.39                  | 2.70                 | 2.70                 | 2.34   | 2.34                                 | 2.34                   | 2.34                   | 2.34                   | 2.34                  | 2.34     |
| $f_{r'}$    | 0.34                 | 0.27              | 0.19                                | 0.35                 | 0.39                | 0.39                  | 0.35                 | 0.35                 | 0.35   | 0.35                                 | 0.35                   | 0.35                   | 0.35                   | 0.35                  | 0.35     |
| $f_{r'ad}$  | 0.28                 | 0.28              | 0.19                                | 0.35                 | 0.39                | 0.39                  | 0.35                 | 0.35                 | 0.35   | 0.35                                 | 0.35                   | 0.35                   | 0.35                   | 0.35                  | 0.35     |

Table 5. Thermodynamic properties of SF<sub>4</sub>O

| T, K   | Cp°, cal/mol | H°-H <sub>0</sub> °, kcal/mol | -(F°-h <sub>0</sub> °)/T, cal/(mol deg) | S°, cal/(mol deg) |
|--------|--------------|-------------------------------|---|-------------------|
| 0      | 0            | 0                             | 0                                       | 0                 |
| 100    | 10.185       | 0.861                         | 50.332                                  | 58.946            |
| 200    | 15.546       | 2.138                         | 56.890                                  | 67.580            |
| 298.15 | 20.314       | 3.910                         | 61.611                                  | 74.726            |
| 300    | 20.388       | 3.948                         | 61.692                                  | 74.852            |
| 400    | 23.683       | 6.163                         | 65.794                                  | 81.202            |
| 500    | 25.849       | 8.647                         | 69.442                                  | 86.736            |
| 600    | 27.301       | 11.309                        | 72.737                                  | 91.585            |
| 700    | 28.303       | 14.092                        | 75.742                                  | 95.873            |
| 800    | 29.016       | 16.960                        | 78.502                                  | 99.702            |
| 900    | 29.538       | 19.889                        | 81.052                                  | 103.151           |
| 1000   | 29.929       | 22.863                        | 83.421                                  | 106.285           |
| 1100   | 30.229       | 25.872                        | 85.632                                  | 109.152           |
| 1200   | 30.463       | 28.907                        | 87.703                                  | 111.792           |
| 1300   | 30.650       | 31.963                        | 89.651                                  | 114.238           |
| 1400   | 30.800       | 35.036                        | 91.490                                  | 116.516           |
| 1500   | 30.923       | 38.122                        | 93.230                                  | 118.645           |
| 1600   | 31.025       | 41.220                        | 94.882                                  | 120.644           |
| 1700   | 31.110       | 44.327                        | 96.453                                  | 122.527           |
| 1800   | 31.182       | 47.441                        | 97.951                                  | 124.308           |
| 1900   | 31.243       | 50.563                        | 99.383                                  | 125.995           |
| 2000   | 31.296       | 53.690                        | 100.754                                 | 127.599           |
| 2100   | 31.341       | 56.821                        | 102.069                                 | 129.127           |
| 2200   | 31.381       | 59.958                        | 103.333                                 | 130.586           |
| 2300   | 31.415       | 63.097                        | 104.548                                 | 131.982           |
| 2400   | 31.446       | 66.241                        | 105.719                                 | 133.320           |
| 2500   | 31.473       | 69.386                        | 106.849                                 | 134.604           |
| 2600   | 31.497       | 72.535                        | 107.941                                 | 135.839           |
| 2700   | 31.518       | 75.686                        | 108.996                                 | 137.028           |
| 2800   | 31.538       | 78.839                        | 110.018                                 | 138.174           |
| 2900   | 31.555       | 81.993                        | 111.008                                 | 139.281           |
| 3000   | 31.571       | 85.150                        | 111.968                                 | 140.351           |
| 3100   | 31.585       | 88.307                        | 112.901                                 | 141.387           |
| 3200   | 31.598       | 91.466                        | 113.807                                 | 142.390           |
| 3300   | 31.609       | 94.627                        | 114.688                                 | 143.362           |
| 3400   | 31.620       | 97.788                        | 115.545                                 | 144.306           |
| 3500   | 31.630       | 100.951                       | 116.380                                 | 145.223           |
| 3600   | 31.639       | 104.114                       | 117.193                                 | 146.114           |
| 3700   | 31.647       | 107.279                       | 117.987                                 | 146.981           |
| 3800   | 31.655       | 110.444                       | 118.761                                 | 147.825           |
| 3900   | 31.662       | 113.609                       | 119.517                                 | 148.647           |
| 4000   | 31.669       | 116.776                       | 120.255                                 | 149.449           |
| 4100   | 31.675       | 119.943                       | 120.977                                 | 150.231           |
| 4200   | 31.680       | 123.111                       | 121.682                                 | 150.995           |
| 4300   | 31.686       | 126.279                       | 122.373                                 | 151.740           |
| 4400   | 31.691       | 129.448                       | 123.049                                 | 152.469           |
| 4500   | 31.695       | 132.617                       | 123.710                                 | 153.181           |
| 4600   | 31.699       | 135.787                       | 124.359                                 | 153.878           |
| 4700   | 31.704       | 138.957                       | 124.994                                 | 154.559           |
| 4800   | 31.707       | 142.128                       | 125.617                                 | 155.227           |
| 4900   | 31.711       | 145.299                       | 126.228                                 | 155.881           |
| 5000   | 31.714       | 148.470                       | 126.827                                 | 156.521           |
| 5100   | 31.717       | 151.642                       | 127.416                                 | 157.149           |
| 5200   | 31.720       | 154.813                       | 127.993                                 | 157.765           |
| 5300   | 31.723       | 157.986                       | 128.561                                 | 158.370           |
| 5400   | 31.726       | 161.158                       | 129.118                                 | 158.963           |
| 5500   | 31.728       | 164.331                       | 129.666                                 | 159.545           |
| 5600   | 31.731       | 167.504                       | 130.205                                 | 160.116           |
| 5700   | 31.733       | 170.677                       | 130.735                                 | 160.678           |
| 5800   | 31.735       | 173.850                       | 131.256                                 | 161.230           |
| 5900   | 31.737       | 177.024                       | 131.768                                 | 161.772           |
| 6000   | 31.739       | 180.198                       | 132.273                                 | 162.306           |

by the following model. The bonding of the three equatorial ligands, ignoring the second bond of the S=O double bond, is mainly due to an  $sp^2$  hybrid, whereas the bonding of the two axial SF bonds involves one delocalized  $p$ -electron pair of the sulfur atom for the formation of a semi-ionic three-center four-electron  $po$  bond [36–38]. The incorrectness of the assignments previously made [9] by Cleveland and coworkers is also reflected by their force field which resulted in significantly stronger axial ( $f_R = 5.54$  mdyne/Å) than equatorial ( $f_E = 4.40$  mdyne/Å) SF bonds, contrary to the electron diffraction data [3–5].

The S—O stretching force constant increases with both increasing oxidation state of the central atom and increasing fluorine substitution. The equatorial S—F stretching force constants also tend to increase for the same sulfur oxidation state with increasing fluorine substitution, except for SF<sub>4</sub>O → SF<sub>6</sub>. Provided the given force constants differences are meaningful, the latter effect might be explained by the higher  $s$ -character of the equatorial SF bonds in SF<sub>4</sub>O ( $sp^2$ ) when compared to those in SF<sub>6</sub> ( $sp^3d^2$ ). Comparison between the stretching force constants of SF<sub>4</sub>O and SF<sub>6</sub> shows good agreement, the slight increase from SF<sub>4</sub> to SF<sub>4</sub>O being attributable to the increase of the sulfur oxidation state.

**Thermodynamic properties.** In view of the absence of thermodynamic data for SF<sub>4</sub>O in the literature and of their interest for chemical lasers, we have computed thermodynamic properties for SF<sub>4</sub>O (see Table 5). The molecular geometry and frequencies from the above force field computation were adopted assuming  $\nu_6 = 475$  cm<sup>-1</sup> and an ideal gas at 1 atm pressure and using the harmonic-oscillator rigid-rotor approximation [39]. It should be kept in mind, however, that the frequencies of two fundamentals ( $\nu_4$  and  $\nu_6$ ) are uncertain and that the sum of the frequencies may therefore be in error by as much as 200 cm<sup>-1</sup>.

#### SUMMARY

The vibrational spectra of pure SF<sub>4</sub>O have been recorded. Out of the 12 fundamentals expected for symmetry C<sub>2v</sub>, 10 have been observed and the previous assignments [9] were revised for 8 of the fundamentals. As for SF<sub>6</sub>, the assignments for the A<sub>1</sub> equatorial SF<sub>2</sub> scissoring and the A<sub>2</sub> torsional mode present difficulties. A systematic study of the vibrational spectra of the presently known pseudo-trigonal bipyramidal fluorides and oxyfluorides is desirable to support the assignments for the deformation modes. The results of a normal coordinate

analysis indicate that the proposed assignments for SF<sub>4</sub>O are plausible. The stretching force constants of SF<sub>4</sub>O are in good agreement with those found for SF<sub>6</sub> and similar molecules. The large difference in the values of the equatorial and the axial SF<sub>2</sub> stretching force constants indicates that model B (or possible C) of GUNDERSEN and HEDBERG are more probable than their preferred model A.

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Vibrational spectra of thionyl tetrafluoride, SF<sub>4</sub>O

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Fig. 4. Definition of internal coordinates.

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SHORT COMMUNICATION

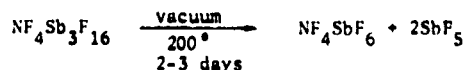
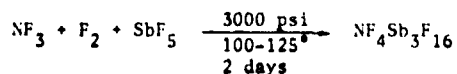
Improved Syntheses of  $\text{NF}_4\text{BF}_4$  and  $\text{NF}_4\text{SbF}_6$

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In view of the importance of  $\text{NF}_4^+$  salts for solid propellant  $\text{NF}_3\text{-F}_2$  gas generators [1], improved syntheses of  $\text{NF}_4\text{BF}_4$  and  $\text{NF}_4\text{SbF}_6$  were required.

Two methods have previously been reported for the synthesis of  $\text{NF}_4\text{SbF}_6 \cdot x\text{SbF}_5$  involving the use of either high pressure and temperature [2,3] or uv-irradiation [4]. Of these, the thermal method is more convenient for larger scale production. According to Tolberg et al. [2,3] the most favorable reaction conditions are:

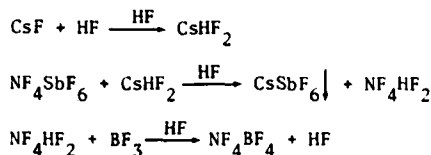


The resulting product contained an appreciable amount of Monel salts and was removed from the reactor by cutting it open with a hacksaw and scraping out the hard clinkered product. Based on recent work done in our laboratory [1], temperatures ( $250-260^\circ$ ), higher than those reported by Tolberg, are required for the vacuum pyrolysis of  $\text{NF}_4\text{SbF}_6 \cdot x\text{SbF}_5$  to  $\text{NF}_4\text{SbF}_6$  within a reasonable time period.

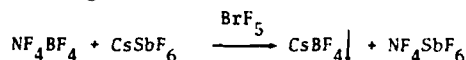
We have now found that most of the drawbacks of the above procedure can be avoided by directly synthesizing  $\text{NF}_4\text{SbF}_6$ . For this purpose,  $\text{NF}_3$ ,  $\text{F}_2$ , and  $\text{SbF}_5$  in a 2:2:1 mol ratio are heated in a Monel cylinder to  $250^\circ$  for 72 hours. The size of the cylinder is chosen in such manner that at the completion of the reaction the autogenous pressure is about 70 atm. The excess of  $\text{NF}_3$  and  $\text{F}_2$  is removed under vacuum at room temperature and the desired  $\text{NF}_4\text{SbF}_6$

product is extracted from the Monel cylinder with anhydrous HF using about 50 ml of liquid HF per 100 g of  $\text{NF}_4\text{SbF}_6$ . Since, contrary to a previous report [3], the formed Monel salt impurities (about 5%) are quite insoluble in anhydrous HF, they can be easily removed from the product by incorporating a porous Teflon filter (Pall Corporation) into the HF solution transfer line. Based on elemental and spectroscopic analyses and the observed material balances, the resulting product was shown to be essentially pure  $\text{NF}_4\text{SbF}_6$ .

Several methods have previously been reported for the synthesis of  $\text{NF}_4\text{BF}_4$ . This salt can be prepared either directly from  $\text{NF}_3$ ,  $\text{F}_2$ , and  $\text{BF}_3$  using glow discharge [5,6], bremsstrahlung [7] or ultraviolet radiation [4,8], or indirectly from  $\text{NF}_4\text{SbF}_6$  using a metathetical process [3,9]. Of these, the metathetical process is most amenable to the larger scale production of  $\text{NF}_4\text{BF}_4$  utilizing existing technology. The original metathetical  $\text{NF}_4\text{BF}_4$  process [3] involved the following steps:



Since the crude product, thus obtained, contained much  $\text{CsSbF}_6$ , its  $\text{NF}_4\text{BF}_4$  content was increased by extraction with  $\text{BrF}_5$ . The use of  $\text{BrF}_5$  resulted in the following side reaction:



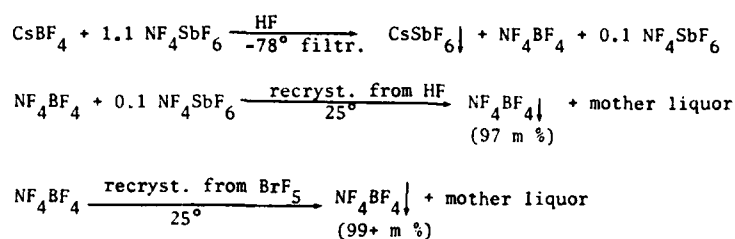
The composition of the final product was reported [3] to be: 91.5%  $\text{NF}_4\text{BF}_4$  and 8.5%  $\text{NF}_4\text{SbF}_6$ . In addition to the requirement of  $\text{BrF}_5$  as a recrystallization solvent, this process suffers from the following disadvantage. Highly concentrated solutions of  $\text{NF}_4\text{HF}_2$  in HF are unstable decomposing to  $\text{NF}_3$ ,  $\text{F}_2$ , and HF. This can cause a pressure build up in the metathesis apparatus which in turn can render filtration steps more difficult.

This process was somewhat improved upon [9] by substituting CsF by AgF. This modification eliminated the  $\text{BrF}_5$  extraction step and resulted in a product of the composition (mol %):  $\text{NF}_4\text{BF}_4$  (89),  $\text{NF}_4\text{Sb}_2\text{F}_{11}$  (7.9),  $\text{AgBF}_4$  (3.1). However, the process still involved the handling of concentrated  $\text{NF}_4\text{HF}_2$  solutions. Furthermore, the cost of silver salts is rather high and therefore requires their recycling in high yields.

We have now found that  $\text{NF}_4\text{BF}_4$  of at least 97 mol % purity can be prepared by a simpler process using anhydrous HF at different temperatures as the only solvent. Furthermore, we have shown that the purity of the  $\text{NF}_4\text{BF}_4$

can be raised to above 99 mol % by a single recrystallization from  $\text{BrF}_5$ . The cesium content in both products was shown to be less than 0.1 mol %, the principal impurity being  $\text{NF}_4\text{SbF}_6$ .

Our improved process consists of the following steps:



The important features of our process are:

- (i) The use of  $\text{CsBF}_4$  instead of  $\text{CsHF}_2$  eliminates one step and avoids the complications caused by  $\text{NF}_4\text{HF}_2$ .
- (ii) The use of a 10 mol % excess of  $\text{NF}_4\text{SbF}_6$  decreases the solubility of  $\text{CsSbF}_6$  by the common ion effect.
- (iii) Carrying out the  $\text{CsSbF}_6$  filtration step at  $-78^\circ$  decreases the  $\text{SbF}_6^-$  concentration since the solubilities of  $\text{SbF}_6^-$  salts in anhydrous HF decrease with decreasing temperature much more rapidly than those of  $\text{BF}_4^-$  salts. Furthermore, the amount of  $\text{NF}_4\text{BF}_4$ , retained in the  $\text{CsSbF}_6$  filter cake by absorption of a certain volume of mother liquor, is minimized owing to the decreased solubilities.
- (iv) Since  $\text{NF}_4\text{BF}_4$  and  $\text{NF}_4\text{SbF}_6$  have comparable solubilities in HF at room temperature, the 10% excess of  $\text{NF}_4\text{SbF}_6$  used in the  $\text{CsSbF}_6$  precipitation step can be removed as mother liquor by recrystallization from HF at room temperature. Unfortunately, the solubilities in HF at room temperature are so high that a significant percentage of the mother liquor is retained by the  $\text{NF}_4\text{BF}_4$  precipitate. This problem can be minimized by using for this recrystallization a solvent in which these  $\text{NF}_4^+$  salts are less soluble. Thus, a single recrystallization from  $\text{BrF}_5$  raised the product purity above the 99 mol % level. Other suitable solvents could be used to replace  $\text{BrF}_5$  in this step. The mother liquors of the recrystallization steps can be easily recycled into the  $\text{CsSbF}_6$  precipitation step, thus avoiding the loss of any  $\text{NF}_4^+$  values.

In summary, the combination of the two improved processes for the syntheses of  $\text{NF}_4\text{SbF}_6$  and  $\text{NF}_4\text{BF}_4$ , respectively, results in a relatively

simple and economical process for the production of  $\text{NF}_4\text{BF}_4$  in a purity of about 97 mol %. Furthermore, it was demonstrated for the first time that high purity (99+ mol %)  $\text{NF}_4\text{BF}_4$  can be prepared by metathesis.

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## IGNITION TEST - GASEOUS $F_2$ - $NF_3$ ON MAGNETIC RECORDING TAPE

A sample of standard 1" wide, 6" long, 1-mil thick polyester magnetic recording tape (Ampex Catalog No. 787-57G11A-GS FSN5835-168-9522 per specification WT001553) was subjected to a short burst of gaseous  $F_2/NF_3$  to determine the hypergolicity (ignition) characteristics of the system. The reaction was spontaneous and rapid with the tape bursting into flame immediately. The tape sample was placed in a windowed combustion chamber (as shown in Fig. 1). The  $F_2/NF_3$  gases were those generated from burning  $NF_4BF_4/KF/Hg$  grains and contained in a 1-gallon Hoke cylinder at approximately 500 psi. The actual gas composition is presented in Table I. The test system was plumbed as shown in Fig. 1 using 1/2" diameter stainless steel lines and air-operated 1/2" diameter Worthington Model 9420 control valves with  $GN_2$  operators. Test procedure was as follows:

- 1) Tape sample was inserted into the window bomb and held in place with a standard strand sample holder.
- 2) After closing the bomb assembly and checking for leaks with  $GN_2$  (by backfilling thru the vent valve) the vent valve was closed.
- 3) The hand valve on the Hoke cylinder was opened and the test cell closed.
- 4) The fill valve was remotely opened while viewing the window bomb thru the test cell window. The fill valve was cycled on and off as quickly as possible. Immediately after opening the fill valve, visible flames were apparent in the window bomb.
- 5) Visible flame died out in a few seconds and the vent valve was opened, initiating more visible flame in the window bomb as gaseous flow out of the window bomb occurred. These flames soon died out.
- 6) The vent valve was closed and the fill valve again cycled quickly on and off. Visible flame was again spontaneous and immediate, only this time the gasket (Teflon) on the window also burned, causing visible flame to spew out around the window.



# IGNITION TEST - GASEOUS $F_2$ - $NF_2$ ON MAGNETIC RECORDING TAPE

- 7) The vent valve was opened and left open to permit venting of the bomb to ambient pressure.
- 8) After approximately one hour, the hand valve on the Hoke cylinder was closed and the top of the window bomb was removed. The tape sample was completely consumed. The window gasket was badly burned, ruining the gasket and the window. (Replacements are available.)

Surprisingly enough, a magnesium-Teflon ignition pellet placed in a nickel crucible in the bottom of the window bomb was not burned during these tests. The pellet was removed from the bomb after the test, slightly scorched, but it obviously did not ignite.

No pressure measuring device was utilized in these tests. However, the estimated pressure in the window bomb was less than 100 psi since the fill valve was open a very short time and pressure equilibrium with the Hoke cylinder reservoir almost certainly did not occur.

This test data indicates that utilization of gases generated from  $NF_4BF_4$  containing grains is a viable method of rapidly destroying magnetic tape and probably almost any other stored data housed in a suitable container so that gas flow across the material is ensured.

TABLE I. GAS ANALYSIS OF GASES IN HOKE CYLINDER

| <u>Gas</u>         | <u>Mole %</u> |
|--------------------|---------------|
| $NF_3$             | 47.3          |
| $F_2$              | 38.3          |
| He                 | 8.3*          |
| $N_2$              | 2.8           |
| $BF_3$             | 2.1           |
| HF                 | 0.4           |
| CF <sub>4</sub>    | 0.2           |
| CF <sub>3</sub> OF | 0.3           |
| COF <sub>2</sub>   | 0.1           |
| O <sub>2</sub>     | 0.1           |
| Unknown            | 0.1           |

\*The He value is probably too high as a result of the gas sampling procedure.

# IGNITION TEST - GASEOUS $F_2-NF_3$ ON MAGNETIC RECORDING TAPE

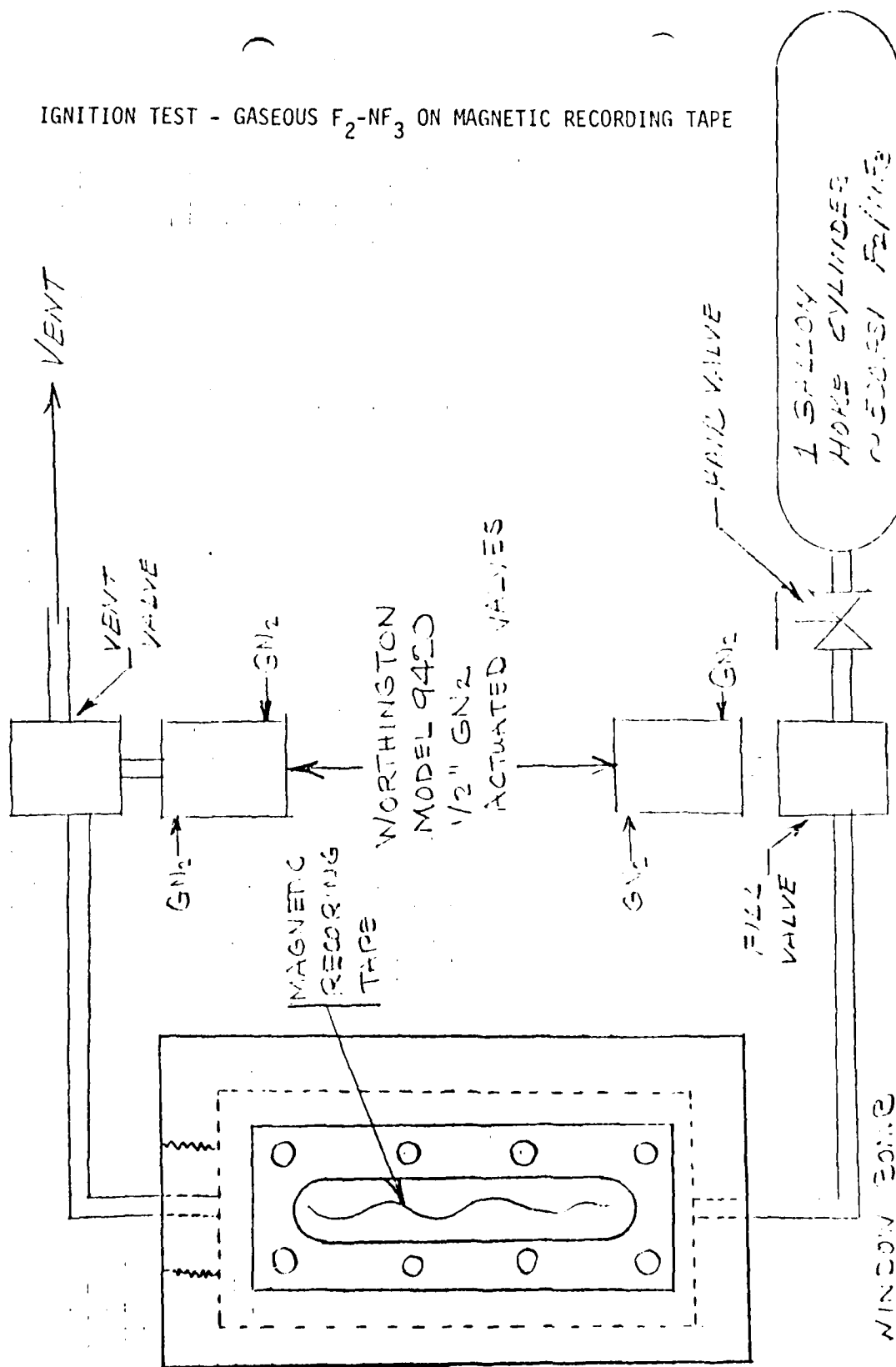


FIGURE 1: TEST SETUP FOR IGNITION TEST